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REDUCTION OF ATMOSPHERIC POLLUTION

FINAL REPORT ON RESEARCH ON REDUCING EMISSION OF SULPHUR OXIDES, NITROGEN OXIDES, AND PARTICULATES BY USING FLUIDISED COMBUSTION OF COAL

Main Report (Vol. 1 of 3)

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The aim was to determine the usefulness of the fluidised combustion system in reducing the emission of sulphur and nitrogen oxides, and particulates from the combustion of coal. The following work was involved: (1) experiments on a number of pilot-scale combustors to measure the effect on emission of sulphur and nitrogen oxides and particulates of a selected range of process conditions, e.g. (a) coal type, (b) the quantity, size and type of additive (limestone/dolomite) fed to the combustor to retain sulphur, (c) combustion conditions as regards temperature, pressure and fluidising velocity, (d) plant scale, and (e) design features such as bed depth and the recycling of incompletely reacted fuel and additive; (2) experiments on selected pilot-scale combustors to assess the extent to which the addition of limestone or dolomite to coal in a fluidised bed in a large test rig influences the corrosion, erosion and deposit formation on specimens representative of typical evaporator, superheater and reheater tube metals; (3) laboratory scale experiments to characterise the coals and additives used; and (4) development of a mathematical model to assist in correlating the factors influencing the pollution control characteristics of a fluidised combustion system. Experiments were carried out at combustion pressures up to 5 atmospheres absolute, fluidising velocities up to 11 ft/s, bed temperatures up to 1680°F, using four different coals, three limestones and two dolomites, and the test running time totalled 5,300 hours.

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CONTROL GROUP

NATIONAL COAL BOARD
LONDON, ENGLAND

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FOREWORD

This document describes studies carried out by the National Coal Board of the U.K. and jointly financed by the NCB and the National Air Pollution Control Administration (now the Office of Air Programs) of the U.S. Environmental Protection Agency. The work was performed over the period June 1970 to June 1971 at the NCB research establishments at Cheltenham (CRE) and Leatherhead (BCURA). The Contract Manager for the Office of Air Programs was Mr. P.P. Turner and the OAP representative in the U.K. was Mr. E.L. Carls.

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The appendices are bound in two separate volumes: Appendices 1. 2. and 3 in one volume; Appendices 4. 5. 6. 7. 8, and 9 in another.

SUMMARY AND CONCLUSIONS

Scope of the Programme

The U.K. National Coal Board (NCB) and the U.S. National Air Pollution Control Administration (NAPCA - now the Office of Air Programs, OAP) entered into an Agreement starting on June 1st 1970, jointly to sponsor a programme of research to determine the usefulness of the fluidised combustion system in reducing the emission of sulphur and nitrogen oxides, and particulates from the combustion of coal.

The programme was scheduled to cover a period of twelve months and involved the following work at the NCB's Leatherhead and Cheltenham laboratories:

(i) Experiments on a number of pilot-scale combustors to measure the effect on emission of sulphur and nitrogen oxides and particulates of a selected range of process conditions, e.g. (a) coal type, (b) the quantity, size and type of additive (limestone/dolomite) fed to the combustor to retain sulphur, (c) combustion conditions as regards temperature, pressure and fluidising velocity, (d) plant scale, and (e) design features such as bed depth and the recycling of incompletely reacted fuel and additive.

(ii) Experiments on selected pilot-scale combustors to assess the extent to which the addition of limestone or dolomite to coal in a fluidised bed in a large test rig influences the corrosion, erosion and deposit formation on specimens representative of typical evaporator, superheater and reheater tube metals.

(iii) Laboratory scale experiments to characterise the coals and additives used.

(iv) Development of a mathematical model to assist in correlating the factors influencing the pollution control characteristics of a fluidised combustion system.

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The features of the combustors used, the range of operating conditions explored, and the aggregate number of test hours accomplished are shown in Tables S.1 and S.2. It will be noted that experiments were carried out at combustion pressures up to 5 atmospheres absolute, fluidising velocities up to 11 ft/s, bed temperatures up to 1680°F, using four different coals, three limestones and two dolomites, and ~~that~~ the test running time totalled 5,300 hours.

Table S1

Main Features of the Pilot-Scale Combustors

Location	BCURA, Leatherhead		CRE, Cheltenham		
Designation	27 in	48 in x 24 in (pressurised)	36 in	12 in (corrosion)	6 in
Bed Cross Section	27 in dia	48 in x 24 in	36 in x 18 in	12 in x 12 in	6 in dia
Bed Depth ft	1.5 - 2	3.5 - 4	2 - 7	2	2 - 3
Operating Pressure Atm.Abs.	1	up to 5	1	1	1
Fluidising Velocity ft/s	6 - 11	2	2 - 8	3	2 - 3
Coal Rate lb/h	200 - 300	300 - 500	75 - 300	20 - 25	4 - 6
Total Running Hours	2150	430	1000	1100	600

Table S2

The Variables Explored

Operating Variables	Pilot-Scale Combustor(s)	
	Non-Pressurised	Pressurised
Coal	U.S. Pittsburgh U.S. Illinois U.K. Welbeck U.K. Park Hill	U.S. Pittsburgh U.K. Welbeck
Ash Content %	12 - 18	13 - 18
Volatile Matter %	37 - 47	30 - 41
Sulphur %	1.3 - 4.4	1.3 - 3.1
Chlorine %	0.1 - 0.6	0.1 - 0.6
H_2O as fed %	1 - 10	1 - 6
Ash Fusion °F	1800 - >2600	2100 - 2600
Size	-1/8 in and -1/16 in	-1/16 in
Bed Depth ft	1.5 - 7	3.5 - 4
Temperature °F	1420 - 1680	1470
Fluidising Velocity ft/s	2 - 11	2
Excess Air %	-12 to +29	11 to 33
Recycle of Cylone Fines	Zero, Partial, Full	Partial
Additive	U.S. Limestone 18 U.S. Limestone 1359 U.K. Limestone U.S. Dolomite 1337	U.S. Limestone 18 U.S. Dolomite 1337 U.K. Dolomite
Ca/S mol ratio	0 - 6	0 - 3

Main Conclusions

The main conclusions reached from the work are :-

(i) That with fluidised combustion and the addition of limestone (or dolomite) the emission of sulphur oxides from coal burning power plant can readily be controlled to meet the very rigorous restrictions (100 ppm v/v SO_2) planned for certain densely populated areas in the U.S. For a power plant burning a 3% sulphur coal this would involve feeding sufficient additive to retain 95% of the sulphur. Under the best combinations of operating conditions about 1.8 times the stoichiometric quantity of additive would be required which for a 100 MW plant would involve supplying 160 ton/day of limestone or 280 ton/day of dolomite. The less stringent restrictions that have been proposed for built-up areas (300 ppm), and for power stations generally in the U.S. (700 ppm), would require sulphur retentions of 85% and 67% respectively for 3% sulphur coals. These limits can be met under a wider range of operating conditions and/or at less expense for additives.

(ii) That emission of oxides of nitrogen from fluidised combustion systems can be expected to be at least 60% less than from conventional combustion systems but additional measures would be needed over and above those used for SO_2 reduction to meet the very stringent restrictions envisaged for the latter part of the century (i.e. 100-200 ppm).

(iii) That the particulates emitted from fluidised bed systems are unlikely to cause problems in meeting current or possible future restrictions.

(iv) That the use of limestone/dolomite additive to restrict sulphur emission is unlikely to affect adversely the exemplary behaviour of the fluid bed combustion system from the point of view of (a) fouling and corrosion of tubes immersed in the bed and (b) deposition or erosion of turbine blade materials exposed to the combustion gases.

The Effect of Operating Variables on SO_2 Emission

Pittsburgh coal (3% sulphur) was used with either Limestone 18 or Dolomite 1337 in the majority of the experiments. Whilst it is believed that most of the comments in the following statement of the main findings apply to other coals and additives, they refer primarily to these materials unless otherwise stated.

The order in which the operating variables are commented upon takes into account both their relative importance and some of the interactions, e.g. through their effect on gas and solids residence times.

Since there was no significant difference in the SO_2 emission from the different combustors when operating under comparable conditions, it has been concluded that differences in scale and design features could in general be ignored when considering the effects of changing the variables

Ca/S mol ratio: The SO_2 is reduced asymptotically to zero as the feed rate of additive to the fluidised bed is increased The percentage SO_2 reduction obtained at a given operating condition is a function of the molar ratio of added calcium to sulphur in coal, and is almost independent of the sulphur content of the coal, since the reaction is approximately first order with respect to SO_2 concentration. Clearly, in order to obtain a specified concentration of SO_2 in the offgas when burning a coal of high sulphur content, it is necessary to achieve a higher percentage SO_2 reduction by using a higher Ca/S mol ratio.

For a given coal the lowest values of the Ca/S mol ratio were required at (i) low fluidising velocities (i.e 2 to 3 ft/s), (ii) a bed temperature of around 1500°F, and (iii) when most of the fines larger than about 10 μm were recycled.

Bed Temperature: The optimum bed temperature was between 1400°F and 1600°F. The level of SO_2 emission and the change in emission with change of temperature on each side of the optimum appeared to depend on the type of additive used and to some extent on the Ca/S ratio employed. The increase in emission on either side of the minimum tended to be greater at low than at high Ca/S ratios, i.e. under conditions where the fraction of calcium sulphated was higher. The optimum temperature was found to be 1500-1550°F for limestone additive and 1400°F-1500°F for the dolomite. The data suggest that to maintain the same level of sulphur emission (e g 85% sulphur retention) at, for example, 100°F above the optimum, would involve increasing the Ca/S ratio by a factor of about two. The effect of changing bed temperature was not investigated on the pressure combustor.

The rapid increase in sulphur emission at bed temperatures above about 1550°F is unexpected from laboratory measurements of the reaction rate between CaO and SO_2. Since the effect of temperature appears to be reversible, i.e. the SO_2 reduction reverts to a high value almost immediately the bed temperature is reduced, it cannot be accounted for by irreversible factors such as sintering or slag formation at the particle surface. One tentative explanation postulates that an oxygen-containing species (e.g. hydroxide ions derived from traces of water, which is known to be difficult to remove) are involved in the conversion of $CaSO_3$ to $CaSO_4$. It is possible that above the optimum temperature the hydroxide ions become more mobile and hence less able to participate in the reaction.

At low temperatures (e.g. below 1350°F) sulphur retention with dolomite was higher than with limestone, the reason being the lower calcination temperature of the $MgCO_3$ in dolomite which leads to the development of pore structure below the temperature of calcination of the $CaCO_3$.

Fluidising Velocity: Increase in fluidising velocity resulted in an increase in sulphur emission. An empirical correlation was derived and is reported later in the summary. Increase in velocity without any compensating action results in reduction in both gas and solids residence times. To maintain the same sulphur retention, say 85%, at 8 ft/s as at 2 ft/s fluidising velocity the Ca/S mol ratio (at a bed temperature of 1500°F and without recycle) would have to be increased from about 2 to about 4.

Bed Height: Increase in bed height usually resulted in a reduction in SO_2 emission. An empirical correlation is reported later in the summary. In principle it should be possible to counteract the adverse effect of increasing velocity by a proportionate increase in bed height. At atmospheric pressure the attendant increase in pressure loss for other than a small increase in bed height could be prohibitive. In addition because the tube bank required would occupy only a part of the bed height the effectiveness of increasing bed height may be reduced by the formation of large gas bubbles. The effect of bed height in supercharged boilers is potentially of greater significance. Here the deep banks of close packed tubes may assist in breaking up large gas bubbles and hence may improve the contact between gas and solids. Further, the increase in pressure loss due to increasing bed height is less important under pressure.

Fines recycle: A high proportion of the additive is elutriated from the bed before being fully utilised. By efficient recycle of fines larger than 10 μm, to the bed, SO_2 reduction was increased significantly, e g from 73% to 99% at a fluidising velocity 2 ft/s and a Ca/S mol ratio of 1.6.

Operating pressure: The effect of operating pressure on SO_2 reduction was negligible when dolomite was used as an additive. This is to be expected with a reaction which is first order with respect to the partial pressure of SO_2 With limestone as an additive, the reduction obtained at 5 atm. was appreciably lower than with dolomite, and lower than with limestone at atmospheric pressure. This was also to be expected, since at 1470°F, calcination of limestone to give a porous structure would not occur at operating pressures above 2 atm. Penetration of the particle by SO_2 would therefore be difficult and only a surface layer of sulphate would form. It was found, however that the performance of the limestone was better than this reasoning would imply, and this suggests that the exposure of fresh surface by attrition plays a significant role. Nevertheless, from the point of view of both the Ca/S mol ratio and the total quantity of additive required to attain a target level of sulphur retention, dolomite was superior to limestone. To retain 85% of the sulphur, for example, the estimated Ca/S mol ratios for dolomite and limestone were 1.1 and 3.25 respectively, and the estimated quantities of additive were, respectively, 7.6 lb and 12 lb per lb of sulphur removed.

Particle Size: It was found for coarsely crushed limestone that the percentage SO_2 reduction increased when the particle size of limestone was reduced, probably due to the consequent increase in available reaction surface On the other hand, with dolomite there was no effect of particle size, suggesting that access to internal surface is not a limiting factor for dolomite.

With additive ground to -125 μm or -150 μm, it was found that the fluidising velocity had a profound effect on SO_2 reduction. Whereas at low velocity (3 ft/s) the fine additive improved SO_2 reduction, the reverse was true at high velocity (8 ft/s). The data of Pope, Evans and Robbins suggest that, with a Ca/S mol ratio of 2.6 in beds 10 in deep fluidised at 12 ft/s, Limestone 1359 gave 80% SO_2 reduction when ground to -44 μm, and 60% reduction when ground to -74 μm. Evidently the SO_2 reduction is very sensitive to the size of finely ground particles, so that the Pope, Evans and Robbins data are at least qualitatively consistent with those for -150 μm limestone from the present study. Limestone ground to -150 μm may have too short a residence time at high velocity to achieve a high degree of sulphation, whilst superfine material will become highly sulphated, since its residence time will not be markedly less than that of -150 μm material. However, superfine material may cause serious gas-cleaning problems.

Type of additive: The type and source of additive affects the reduction in SO_2 that can be achieved. At atmospheric pressure Limestone 18 was the most effective additive on both molar and weight bases; the least effective on a mol basis was Limestone 1359, and on a weight basis Dolomite 1337. To achieve the same level of retention with the poorer Limestone 1359 as with the Limestone 18 would require an increase of up to 100% in the Ca/S mol ratio. As mentioned previously, for operation under pressure, both the dolomites were superior to Limestone 18 on weight and molar bases.

An important finding from the point of view of simplifying prediction of suitability of stones was that measurements made at room temperature and at combustor temperatures showed the same accessibility of the structure to gases of similar molecular size to SO_2 Temperature cycling (as may occur in some plant designs when elutriated particles are recirculated) does not affect the pore structure significantly from the point of view of SO_2 uptake. An empirical reactivity test was considered to be the most economic method for classifying stones. For limestones the results of laboratory experiments give pessimistic predictions of plant performance. This is thought to be because these tests do not take into account the beneficial effect of attrition in the combustor which results in removal of the sulphated surface layer. The effect of attrition was particularly important for limestones in the pressurised combustor and for Limestone 1359 at atmospheric pressure. For dolomite, access to the internal surface of the particles does not appear to be a limiting factor.

Whereas thermal losses are incurred from the sensible heat requirement and the heat of calcination of an additive, the heat of sulphation represents a thermal gain. Up to a Ca/S mol ratio of about 2 using limestone (sufficient to retain 85% of the sulphur of a 3% sulphur coal under good operating conditions) it is estimated that the heat of sulphation will counterbalance the sensible heat requirements and heat of calcination. With dolomite however the nett thermal loss would be about 1½% of the coal heat input. Under pressure, calcination of $CaCO_3$ is inhibited and the thermal loss incurred by using dolomite would be negligible for Ca/S mol ratios up to 2.

Type of coal: The most important coal property in this context is the sulphur content, which determines not only the quantity of additive required for a given Ca/S mol ratio, but also the percentage SO_2 reduction (and hence Ca/S mol ratio needed) to meet set limits of SO_2 emission. Since the SO_2 absorption reaction is first order with respect to SO_2 concentration, it could be expected that the same relationship between percentage reduction and Ca/S mol ratio would hold for all coals irrespective of the sulphur content. However, the experimental results showed that, for a given Ca/S mol ratio, similar SO_2 reductions were obtained for three of the coals, but the reductions were up to 15% higher with Welbeck coal. Differences in the rate of sulphur release have been found between coals and might partly account for differences in performance. A more likely explanation of the higher SO_2 reduction with Welbeck coal is its low sulphur content, which had the consequence that additive was fed at a lower rate and hence had a longer residence time. This could have resulted in the higher degree of sulphation, particularly if particle attrition was an important effect.

Plant design: As mentioned earlier, it was concluded that despite the difference of scale and design over the range of combustors used (Table S1) there was no significant difference between the SO_2 reductions obtained in different combustors with the same operating conditions. Nevertheless, direct application of the present results to combustors of commercial size requires some caution. Some factors which might alter the SO_2 emission, such as the depth of the tube bank, have already been mentioned. Further, observation of a radial distribution of SO_2 concentration in the freeboard of one of the larger pilot plants suggests that coal feed spacing, if greater than that used in the pilot-plants, may assume significance in commercial boilers.

Mathematical model and correlation of data: The mathematical model has been developed to give fairly satisfactory prediction of the consequences of changing some operating conditions. Additional development is needed (a) to take further account of attrition of additive and (b) to extrapolate the results to combustors that differ significantly from the present pilot plants. The model in its present form has not been useful in correlating the experimental data. However a number of empirical correlations have been derived as follows:

There is an approximately exponential relationship between the SO_2 reduction and the Ca/S mol ratio of the form

$$R = 100\ (1 - \exp(-MC)\ )$$

where R is the percentage SO_2 reduction
C is the Ca/S mol ratio
M is an empirical constant depending on the coal, limestone and operating conditions.

The effect of fluidising velocity on SO_2 reduction may be approximately correlated by

$$A = X_1/V$$

where A is the absorption ratio, defined as R/(100-R)
V is the fluidising velocity
X_1 is an empirical constant depending on the Ca/S mol ratio and other operating conditions.

The effect of bed height on SO_2 reduction may be approximately correlated by

$$A = X_2 H$$

where H is the bed height

X_2 is an empirical constant depending on the Ca/S mol ratio and other operating conditions.

Emission of nitrogen oxides

Emission of NO_x from the pressure combustor (50-200 ppm) was significantly lower than from the non-pressurised combustors (300-600 ppm). All the combustors produced less NO_x pollution, both with and without the use of additives, than is common with conventional plant. The reason for the superior performance is uncertain. NO_x emission could not be correlated with SO_2 emission, although on some occasions a decrease in the SO_2 emission (due to feeding limestone or dolomite) was accompanied by an increase in the NO_x emission. It was concluded that more information was needed on the mechanism of NO_x formation before a contribution could be made towards reducing emission.

Emission of alkalis and chlorine

As expected, the low combustion temperatures in fluid bed combustors resulted in low alkali emissions. The combustion gases from the pressure combustor contained about 2 ppm of Na, i.e. about one tenth of the lowest concentration reported for the gases from conventional plant. The concentration of K was less than 0.5 ppm. Higher emissions were measured when limestone was added to the pressurised combustor instead of dolomite (5 ppm of Na and 1.5 ppm of K) and from one of the non-pressurised combustors that was being operated at the higher bed temperature of 1560°F (6 ppm of Na and 3 ppm of K). As expected most of the chlorine of the coal was released into the combustion gases.

Emission of particulates

Particulate matter elutriated from fluidised bed combustors comprises 5 to 15% of the carbon and 80 - 100% of the ash and additive. By using primary and secondary cyclones having collection efficiencies of 90% at about 10 μm it was possible to collect 95 - 98% of this material to give dust emissions of 0.2 - 0.6 gr/scf. Within this range the emission was approximately proportional to the feed rate of ash plus additive. Increasing the fluidising velocity increased elutriation from the bed, but because of more efficient cyclone operation with higher gas flow rates there was little effect on emission. Fines recycle in the 36 in combustor increased the dust emission to 1.4 gr/scf. The pressurised combustor had an internal recirculation cyclone in addition to primary and secondary cyclones, and dust emissions in the range 0.05-0.1 gr/scf were obtained.

Based on these results it is unlikely that there would be any problem in meeting projected statutory limitations on particulate emission.

Corrosion and deposition

The addition of limestone or dolomite had no significant effect on corrosion or deposition of tubes in the bed or in the gas space under the range of operating conditions likely to be experienced in a commercial plant.

The amount of material settling on the turbine blade cascade at the outlet of the pressure combustor was slight and was judged to be unlikely to affect turbine performance. There were no signs of sintered deposits or of erosion.

1. INTRODUCTION

The need to reduce air pollution by sulphur dioxide, nitrogen oxides, carbon monoxide, hydrocarbons and particulates resulting from combustion of fossil fuels in power plants, is widely recognised.

Operating techniques are available at the present time to limit carbon monoxide and hydrocarbon emission to acceptable levels. Particulate emission can in most circumstances be limited to currently acceptable levels using conventional, albeit expensive equipment. The situation as regards the emission of sulphur and nitrogen oxides is much less satisfactory. Because of the low concentrations of the pollutants and the large volumes of gas which must be treated, it is at present inherently expensive to remove sulphur oxides. Insofar as nitrogen oxides are concerned there are as yet no commercial processes. An alternative approach is the development of new fuel burning processes in which the emission of pollutants during the combustion process is reduced. One such process which appears to be particularly promising is the combustion of the fuel within a fluidised bed to which limestone or dolomite is added. This process also offers the possibility of reductions in the capital and operating costs of a fluidised bed boiler, compared with conventional plant, due to the following factors:

1. The placing of steam tubes directly in the fluidised bed results in a reduction in tubing requirements because of the higher heat fluxes attainable in the bed.
2. The low bed temperature at which combustion takes place, 1400 - 1700°F, may reduce tube corrosion and fouling.
3. The higher volumetric heat release rates possible in a fluidised bed combustor may permit smaller unit sizes.
4. The low volatilisation of alkalis at fluidised bed operating temperatures may mean that the exhaust gases can be passed through a gas turbine without deleterious effect. This would enable the combustor to be operated at elevated pressures to further reduce the unit size and also to improve the thermodynamic efficiency.

5. Low quality fuels may be burnt in a fluidised bed.

Experimental work on fluidised bed combustion has been in progress since 1965,[1] both in the U.K., at CRE and BCURA, and in the U.S., by Pope, Evans & Robbins and the U.S. Bureau of Mines. The early work was chiefly concerned with combustion efficiency and heat transfer, but since 1969 the anti-pollution aspects have become of major importance. In the U.S., research on this aspect has been co-ordinated and financed by the Air Pollution Control Office (now the Office of Air Programs) of the U.S. Environmental Protection Agency. In addition to Pope, Evans & Robbins and the U.S. Bureau of Mines, other organisations currently carrying out work on fluidised bed combustion for APCO include the Argonne National Laboratory, Esso U.S.A., Consolidation Coal and Westinghouse. The research work up to June 1970 had demonstrated the following:

1. The combustion efficiency of a single stage fluidised bed is in the range 90 to 98%, depending on the operating conditions.

2. The combustibles losses are almost entirely as elutriated carbon particles. On combustion efficiency considerations the emissions of CO and hydrocarbons are negligible.

3. The overall combustion efficiency can be improved to more than 99% by burning the elutriated fines, either by recycle to the main bed or in a separate burn-up cell.

4. The heat fluxes to the steam tubes in the bed are high, as expected.

5. The particulates leaving the boiler are not so fine as when using pulverised fuel, and are more readily removed from the flue gases.

6. The SO_2 emissions are reduced slightly by combustion in an inert fluidised bed.

7. Under some operating conditions, the SO_2 emission can be reduced by more than 95% when limestone is added to the bed.

8. The system pressure can be increased to at least 6 atm without significant reduction in combustion efficiency.

At this stage the data on combustion and heat transfer were reasonably complete, but there were many gaps in the data on reduction of pollution, in particular

1. The effects of the limestone addition rate, bed temperature, fluidising velocity and bed height were not clearly defined. It was not known whether it would be possible to attain the desired SO_2 retention under the operating conditions indicated as being the most economic, i.e. high temperatures and high fluidising velocities.

2. It was not known why there was a variation in the level of percentage sulphur emission from coal to coal at similar operating conditions, nor was this effect predictable.

3. There were few data on the comparative performance of alternative limestones and dolomites.

4. The effect of coal and additive particle size was not known.

5. The effect of fines recycle (containing part-utilised additive) was not clear, since conflicting results had been obtained.

6. The effect of system pressure when feeding limestone or dolomite was not known.

7. There were apparent differences in performance between the 6 in. rigs at ANL and CRE when operated under similar conditions.

8. There were few data from large pilot plants and it was not known whether there would be an increase in the emission of pollutants on scale-up.

9. It was not known whether the addition of limestone to a bed would affect the rate of corrosion of the steam tubes.

As part of the overall research effort towards an understanding of these problems, a programme of research has been carried out at the NCB research establishments at Cheltenham (CRE) and Leatherhead (BCURA) jointly financed by the U.S. Environmental Protection Agency and the NCB. This programme made particular use of the large pilot scale facilities available and also of the NCB's expertise in the fields of corrosion, materials characterisation and mathematical modelling. This document describes the work which was carried out and presents the main results together with an assessment of the information obtained. Details of the individual research programmes carried out are presented in a series of Appendices.

2. THE RESEARCH PROGRAMME

The main objectives of the research programme were

1. To assess the effectiveness of the fluidised bed combustion process, with and without the addition of limestone or dolomite, towards the reduction of SO_2 emission showing, by experiments over a range of operating conditions, those operating parameters that significantly affect the attainment of the immediate target emission (300 ppm v/v) and to indicate how these data may affect plant design.

2. To gather, over the same range of operating conditions, data on the levels of NO_x emission that occur during the combustion process when the SO_2 is partially absorbed by added limestone or dolomite, relating these data to the operating conditions where possible.

3. To measure the particulates elutriated from the fluidised bed combustor in order to provide data for the design of a particulates removal system which will reduce the emissions to atmosphere to an acceptable level.

4. To contribute towards an understanding of the way in which the porous properties of limestone or dolomite affect SO_2 retention under the conditions prevailing in a fluid bed combustor, and to develop a simple method of classifying limestones and dolomites according to their utility for SO_2 retention in the fluidised bed combustion process.

5. To develop a mathematical model of the retention of SO_2 in a fluid bed combustion system to allow the performance of new plant, with respect to SO_2 emission, to be predicted at the design stage from the design and other basic data.

6. To study corrosion of typical steels used in boiler construction when immersed in a fluid bed burning coal, both with and without the addition of limestone/dolomite.

The research programme to meet these objectives was organised as eight Tasks, as follows:

Task	Main Objective	Plant and/or Location
I	To compare the performance of the 36 in rig with that of the 6 in rigs at CRE and Argonne, and to extend the range of operating conditions for which experimental data is available.	36 in combustor CRE.
II	To obtain, for operation under pressure, data on (i) the emission of sulphur and nitrogen oxides and (ii) corrosion/deposition of boiler metal and turbine blade specimens.	48 in x 24 in combustor (pressurised) BCURA.
III	To carry out long-term tests to assess the effect of limestone addition on corrosion of evaporator, superheater and reheater metals immersed in the fluid bed.	27 in combustor BCURA.
IV	To obtain data on corrosion of evaporator, superheater and reheater materials for lower fluidising velocities.	12 in corrosion combustor CRE.
V	To obtain data on sulphur retention for a range of coals and limestones, in particular to allow comparison to be made with the 6 in rig at Argonne.	6 in combustor CRE.
VI	To complete the development of a mathemetical model of sulphur retention and to compare its predictions with the results of laboratory and rig experiments, and to up-date it as appropriate.	Mathematical work BCURA.
VII	To investigate the distribution of sulphur in a range of coals and in the residue from the rigs.	Laboratory work CRE/BCURA.
VIII	To investigate the pore structure and related factors that affect sulphur retention by lime.	Laboratory work BCURA.

3. MATERIALS USED

The experimental work in the programme was carried out using four coals, three limestones and two dolomites.

3.1 Coals

Typical analyses of the four coals are given in Table 3.1.

Table 3.1

Typical Analyses of Coals Used

Coal		Illinois	Pittsburg	Park Hill	Welbeck
Proximate analysis					
Total moisture	% a.r.	9.8	1.6	2.1	4.2
Ash	% a.r.	11.8	13.5	16.5	18.2
Volatile matter	% a.r.	46.6	41.1	39.2	38.3
Ultimate analysis					
Carbon	% d.b.	67.8	71.7	68.2	67.5
Hydrogen	% d.b.	4.5	4.5	4.4	4.3
Nitrogen	% d.b.	1.3	1.4	1.3	1.5
Sulphur	% d.b.	4.4	2.8	2.5	1.3
Oxygen + errors	% d.b.	8.5	4.4	5.3	5.1
Chlorine	% d.b.	0.2	0.1	0.1	0.6
Calorific value (d.a.f.)	(Btu/lb)	14300	15100	14750	14400
Swelling Number		4½	8	1	1
Gray King coke type		D	G9	D	C
Ash Analysis					
CaO	%	10.1	8.0	2.2	1.8
MgO	%	1.0	1.3	1.7	1.4
Na_2O	%	1.7	0.7	0.8	1.8
K_2O	%	1.8	1.6	3.6	3.2
SiO_2	%	40.8	45.8	46.0	57.5
Size					
(As Received)		-¼ in	-¼ in	-1½ in	-1½ in

The sources of the coals were as follows:

Illinois coal: Illinois seam No.6, Peabody Coal Company, Mine 10, Christian County, Illinois: supplied by the Argonne National Laboratory. This coal has been referred to as 'Peabody No.10' or 'Argonne' in interim reports.

Pittsburg coal: Pittsburg seam, high volatile 'A' bituminous coal, Humphrey Preparation Plant, Osage, West Virginia. This coal has been referred to as 'Humphrey No.7' in interim reports.

Park Hill: Yorkshire Coalfield, Park Hill Colliery, Nr. Wakefield.

Welbeck: Midland Coalfield, N.Notts Area, Welbeck Colliery, Nr. Mansfield. Top Hards seam.

3.2 Limestones and dolomites

Typical analyses of the limestones and dolomites are given in Table 3.2.

Table 3.2

Typical analyses of limestones and dolomites

Component	Composition %				
	Dolomite 1337	U.K.dolomite	Limestone 18	Limestone 1359	U.K.limestone
CaO	28.9	29.3	45.7	55.7	55.4
MgO	22.9	21.5	1.4	0.3	0.3
$H_2O + CO_2$	47.4	46.3	36.6	43.6	43.5
SiO_2	0.5	-	13.6	0.5	0.7
Fe_2O_3	0.2	-	0.3	0.1	0.1
SO_3	-	0.1	-	-	-
Total	99.9	97.2	97.6	100.2	99.8

The sources of those materials were:

Limestone 18: Supplied by Fuller Industries Inc., Fort Meyers, Florida. This has been referred to as 'U.S. Limestone No.18' or 'T.18' in interim reports.

Limestone 1359: Supplied by M.J. Grove Lime Co., Stephens City, Virginia and prepared at the Argonne National Laboratory. This has been referred to as 'Argonne' limestone or 'Limestone 1359' in interim reports.

U.K. limestone: Supplied by J. Gregory & Sons, Kidsgrove, Stoke-on-Trent.

U.S. dolomite 1337: Supplied by Charles Pfizer & Co., Gibonsburg, Ohio.

U.K. dolomite: Supplied by Steetley (Manufacturing) Ltd., Worksop, Notts. This has been referred to in interim reports as 'U.K. dolomite' or 'Doloflux'.

4. PILOT PLANT EXPERIMENTAL WORK

The experimental programmes for the pilot plants were sub-divided into test series, each comprising from 1 to 15 tests. The operating conditions in each test series are summarised in Table 4.1. This experimental programme is somewhat different from that given in the research proposals[2], mainly because of late delivery of American coal and limestone. Also additional tests were introduced as the programme proceeded; these changes were agreed with the OAP representative in the U.K.

4.1 Experimental techniques

4.1.1 Measurement of SO_2 concentrations

Three methods have been used for the measurement of the SO_2 concentration in the off-gas from the pilot scale combustors:-

The iodine method

This was the standard method used to determine the SO_2 concentration in all the pilot plant work. Gas was withdrawn from a sample probe by means of a vacuum pump and bubbled through a solution of iodine. The volume of gas required to decolourise a solution of known concentration was measured.

Infra-red analyser

Hartmann-Braun infra-red analysers were used to monitor the SO_2 concentration in Tasks I, II and III. The agreement with the iodine method was good in Tasks II and III, but in Task I the analyser indicated concentrations about 12% lower than those measured by other methods.

The hydrogen peroxide method

This method was used in Tasks I, IV and V as a check on the other methods. Gas was bubbled through a solution of hydrogen peroxide and the sulphate produced was determined gravimetrically by precipitation as barium sulphate.

4.1.2 Measurement of NO_x concentrations

It was intended that infra-red absorption NO_x analysers would be used for this work, but these were not delivered in time to be used. The two methods which were used to determine the concentration of NO_x are described in detail in Appendix 9 and summarised below:

The flue gas sample was withdrawn through a silica probe and bubbled through water to remove SO_2, HCl and other soluble gases. (A steel probe with water injection was used for the pressurised combustor). About 5% of the NO_x was also dissolved in the water, the exact amount being determined using Saltzman's reagent. Two alternative methods were used to determine the remaining NO_x content of the gas.

The modified Saltzman's method

A sample of the SO_2 free gas was taken in an evacuated 400 ml sample bottle containing 40 ml of Saltzman's reagent. After 30 min the solution was withdrawn and fresh reagent was added. This was repeated at intervals of 30 min until the colour developed by the solution was negligible. All of the solution was bulked and the intensity of the colour was measured using a spectrophotometer.

The BCURA NO_x box

In the BCURA NO_x box the SO_2 free gas is first passed through an oxidiser in which any NO present is converted to NO_2. The gas is then passed through a cell containing a platinum gauze electrode moistened by a wick dipping into an electrolyte solution in which an active carbon electrode is immersed. The electrical current through the external circuit between the electrodes is dependent on the NO_2 concentration in the gas, and is measured using a microammeter. Before use the instrument is calibrated using standard gas mixtures.

4.1.3 Measurement of corrosion of metals

The corrosion of metal specimens at various temperatures was investigated under Tasks II, III and IV. Composite tubes were formed by clamping together ⅛ inch wide rings of the metals to be

Table 4.1. Summary of pilot plant research programme
(X, O and Z indicate the operating conditions in each test series)

Task		I								II				
Test Series		1.1	1.2	1.3	2	3	4	5	6	1	2	3	4	5
Coal	Illinois													
	Pittsburgh	X	X	X O	X O		X O	X	X		X	X	X	X O
	Park Hill													
	Welbeck					X				X				
Coal size, μm	-1587 or -1680	X	X	X O			X O			X	X	X	X	X O
	-3175				X O	X		X	X					
Additive	U.K. limestone					X								
	U.K. dolomite									X				
	Limestone 18		X	X O	X O			X						O
	Limestone 1359													
	Dolomite 1337						X O		X		X	X	X	X
Additive size, μm	-125 or -150				O									
	-1587 or -1680		X	X O			X O			X	X	X	X	X O
	-3175				X	X		X	X					
Ca/S mol ratio	0	X	X	X	X	X	X	X	X	X				
	0.5													
	1			X	X O					X				X
	1.5						O	X			X	X	X	
	2		X	X O	X	X	X	X	X		X	X	X	O
	3			X O	X	X	X							
	4								X					
	6							X						
Bed temperature, ^{o}F	1290													
	1380		X				X							
	1470	X	X	O			X O			X	X	X	X	X O
	1560		X	X	X O	X	X	X	X					
	1650													
	1700													
Fluidising velocity, ft/s	2						X O			X	X	X	X	X O
	3			O	O									
	4	X	X	X	O	X	X	X						
	6													
	8				X	X		X	X					
	11													
Bed height, ft.	1.5													
	2	X	X	X O	X O	X	X	X						
	3								X					
	3.5							X						
	3.75									X	X	X	X	X O
	4					X	X O		X					
	6.5								X					
System pressure, atm. abs.	1	X	X	X O	X O	X	X O	X	X					
	3.5									X	X			
	5										X	X	X	X O
Fines recycle	No	X	X	X O	X O	X	X	X	X					
	Yes						O			X	X	X	X	X O

Table 4.1 (continued). Summary of pilot plant research programme
(X, O and Z indicate the operating conditions in each test series)

Task		III				IV			V				
Test Series		1	2	3	4	1	2	3	1	2	3	4	5
Coal	Illinois								X		X O		
	Pittsburgh	X	X O	X O Z	X O	X	X	X				X O	
	Park Hill									O			
	Welbeck									X			X
Coal size, μm	-1587 or -1680					X	X	X	X	X O	X O	X O	X
	-3175	X	X O	X O Z	X O								
Additive	U.K. limestone								X	X O		X	X
	U.K. dolomite												
	Limestone 18		X O	X O	O			X				O	X
	Limestone 1359								X		X O		
	Dolomite 1337			Z	X								
Additive size, μm	-125 or -150		O	O							O		
	-1587 or -1680			Z	X			X	X	X O	X	X O	X
	-3175		X	X	O								
Ca/S mol ratio	0	X	X			X	X		X	X O		X	
	0.5		X		X					O			
	1		X O						X	X O	X O	X O	
	1.5				X					O			
	2		X O	Z				X	X	X	X	X O	X
	3		X O	X O	X O				X	X O	O	X O	
	4		X		X								
	6												
Bed temperature, °F	1290										X		
	1380				X								
	1470	X	X		O				X	X O	X O	X O	X
	1560		X O	X O Z	X	X	X	X					
	1650			X									
	1700				X								
Fluidising velocity, ft/s	2									X			
	3					X	X	X	X	X O	X O	X O	X
	4												
	6			X O									
	8	X	X O	X Z	X O								
	11			X									
Bed height, ft.	1.5		X										
	2	X	X O	X O Z	X O	X	X	X	X	X O	X O	X O	X
	3										X		
	3.5												
	3.75												
	4												
	6.5												
System pressure, atm. abs.	1	X	X O	X O Z	X O	X	X	X	X	X O	X O	X O	X
	3.5												
	5												
Fines recycle	No*		X O	X	X				X	X O	X O	X O	X
	Yes	X	X O	X O Z	X O	X	X	X		X			

* In Task III, no recycle refers only to the external system.

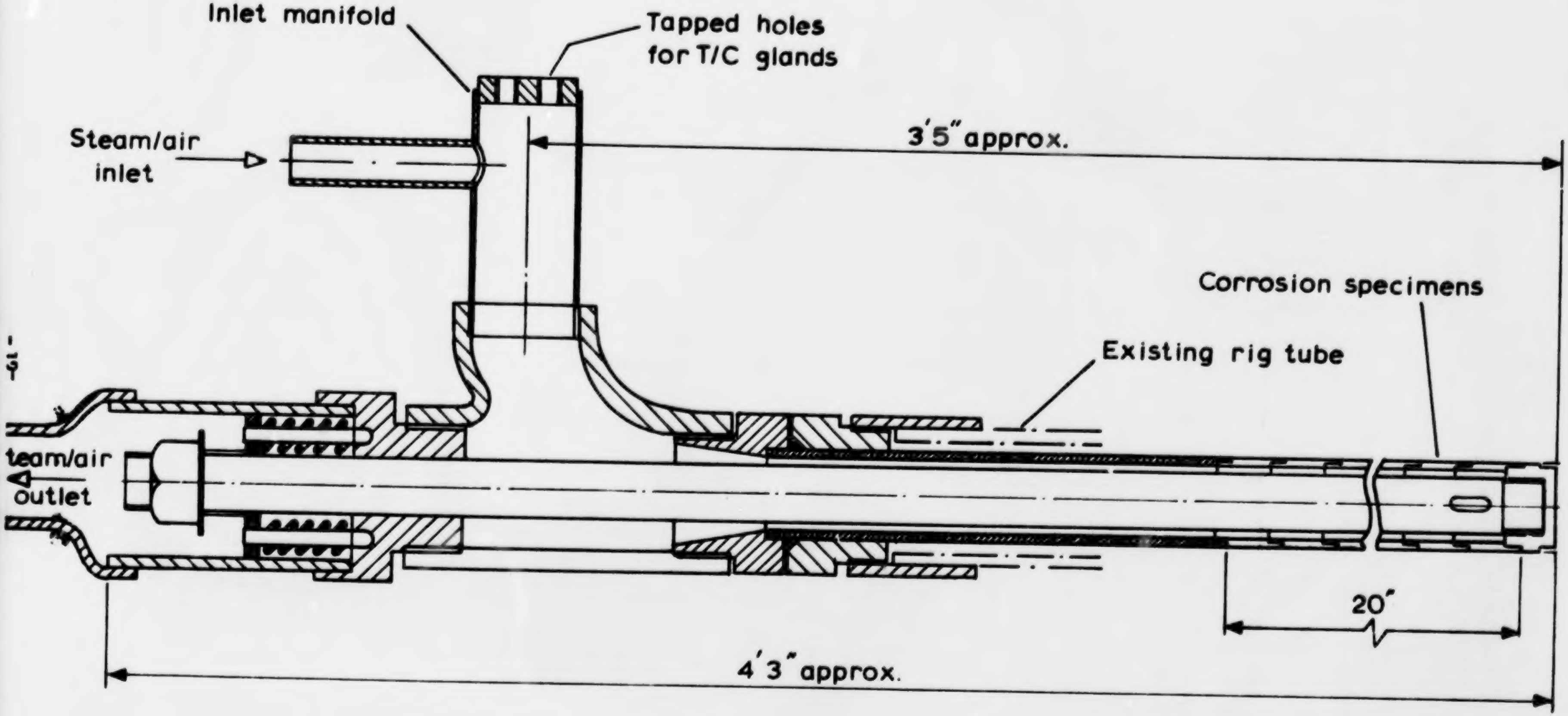

Inlet manifold
Tapped holes for T/C glands
Steam/air inlet
3'5" approx.
Corrosion specimens
Existing rig tube
team/air outlet
20"
4'3" approx.

Fig. 4.1 General arrangement of corrosion tube assembly

examined. The rings were 2 in diameter for Tasks I, III and IV, as shown in Fig. 4.1, and 1 in dia for Task II. The surface of the rings was ground to a smooth finish of 10 μin or better, and each ring was cleaned and weighed before assembly into the tubes. Several such tube assemblies were installed in the fluidised bed and each tube was maintained at a different constant temperature, using air as coolant (or steam in some tests in Task III). Tube wall temperatures were measured using thermocouples inserted into holes drilled in two or three rings on each assembly. In Task IV, cooled tube assemblies were also installed in the freeboard, and uncooled metal plates (coupons) were used, both in the bed and freeboard

After a test the tubes and coupons were removed, photographed and examined visually. Deposits and scales were sampled where they existed and where they could be removed without damaging the metal specimens. Rings and coupons were then selected for more detailed microscopic examination of the fireside surfaces and thickness measuremenets of scale and deposit with a micrometer.

The majority of the test specimens were then descaled by immersing them for five minutes in a bath of molten sodium hydroxide containing 2% of sodium hydride maintained at 680 - 715°F. They were then water quenched and washed to remove all traces of scale. The specimens were then re-weighed and a selection of both descaled and undescaled rings and coupons were sectioned for metallographic examination.

A number of 'blank' determinations were carried out to assess the accuracy of the weight loss determinations. Specimens were weighed and descaled without being exposed in the fluid bed combustors. The results suggested that over a period of 100 hours, weight loss changes of less than 2 $\mu g/cm^2h$ were not significant.

4.2 The 36 in combustor (Task I)

The work carried out on the 36 in combustor is described in detail in Appendix I.

4.2.1 Description of the plant

A flow diagram of the 36 in combustor plant is shown in Fig. 4.2 and the details of the combustor vessel are given in Fig. 4.3. The combustor was a mild steel column with refractory lining, having an internal cross-section of 36 in by 18 in. The air distributor comprised a plate with 1/2 in diameter stand pipes on a 3 in square pitch, each stand pipe having four 0.147 in diameter holes drilled horizontally around the top. The height from the distributor to the gas offtake was 15 ft. Coal and additive were fed pneumatically from separate hoppers through adjacent lines to the centre of the bed cross-section, 5 in above the air jets. The off-gases passed through primary and secondary cyclones and then to the stack. These cyclones were 90% efficient at 12 μm and 9 μm respectively. The primary cyclone fines could be recycled to the bed via an external line, if required. The heat generated in the bed was removed by 14 water-cooled tubes (2 in inside diameter) arranged on a 4½ in triangular pitch within the 2 ft deep zone above the distributor. The water flow-rate was normally controlled automatically to maintain the bed temperature at a set level. The excess heat generated in the free-board was removed by injecting steam, in order to limit the off-gas temperature to a maximum of $1700^{\circ}F$.

The normal operating procedure was to set up an operating condition, allow the system to stabilize and then to carry out a four hour mass balance. The main gas sampling point was after the cyclones, but there were also sampling points in the freeboard. Samples were taken for determination of O_2, CO, CO_2 and CH_4 by chromatograph. SO_2 was determined by bubbling through iodine or hydrogen peroxide solutions and was also continuously monitored using a Hartmann-Braun infra-red analyser. NO_x was measured using Saltzman's method. NH_3 and Cl^- were determined by analysis of the peroxide solution. All the outlet solids streams were sampled and solids samples could also be extracted directly from the bed. The plant was operated without fines recycle except for a single experiment, Test 4.6.

4.2.2 Experimental programme

Tests were carried out using Pittsburgh coal with Limestone 18 and Dolomite 1337, and Welbeck coal with U.K. limestone. Six series

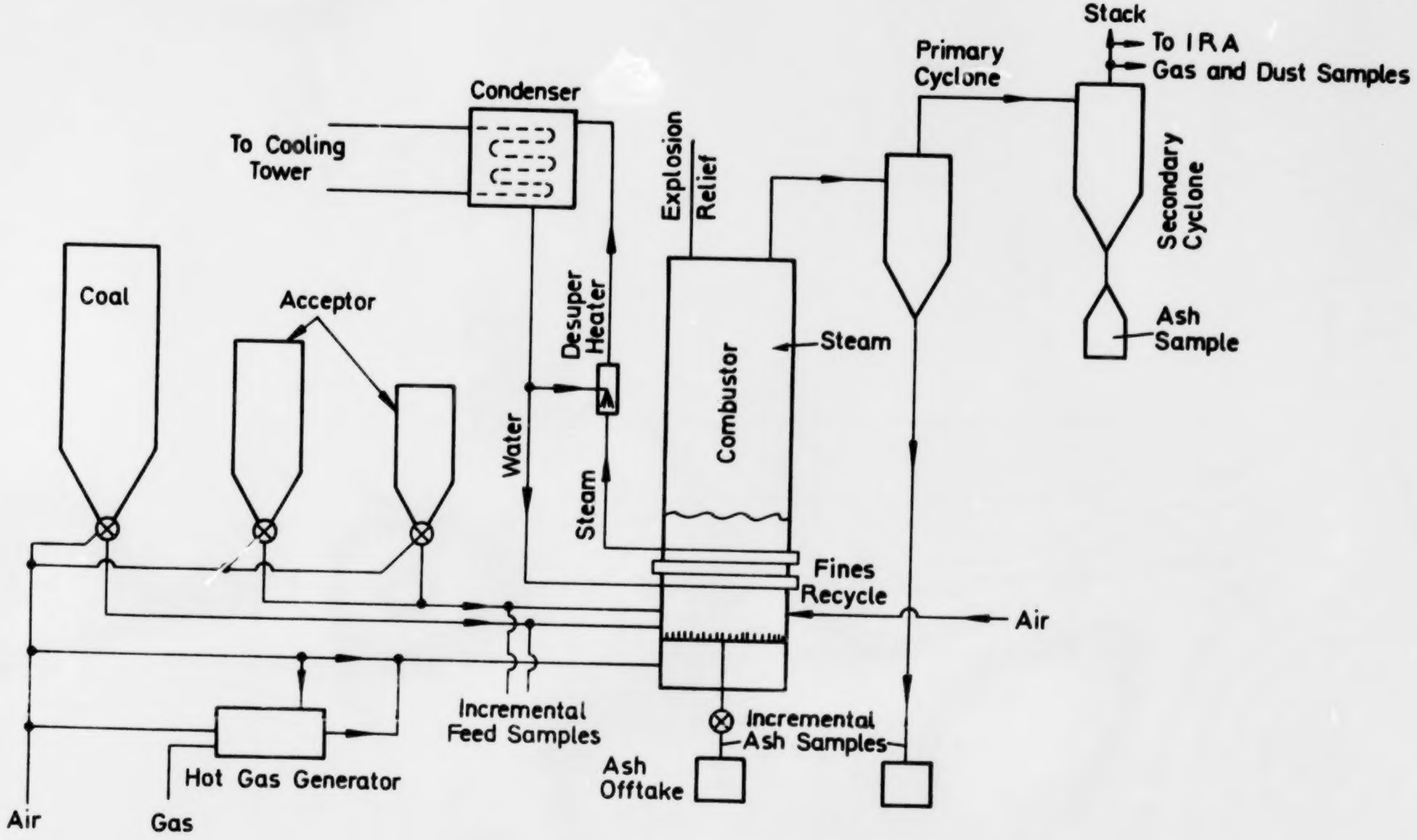

Stack
To I R A
Gas and Dust Samples
Primary Cyclone
Condenser
To Cooling Tower
Explosion Relief
Secondary Cyclone
Coal
Acceptor
Desuper Heater
Steam
Ash Sample
Combustor
Water
Steam
Fines Recycle
Air
Incremental Feed Samples
Incremental Ash Samples
Ash Offtake
Hot Gas Generator
Air
Gas

Fig. 4. 2 Task I. Flow diagram of 36 in. combustor plant

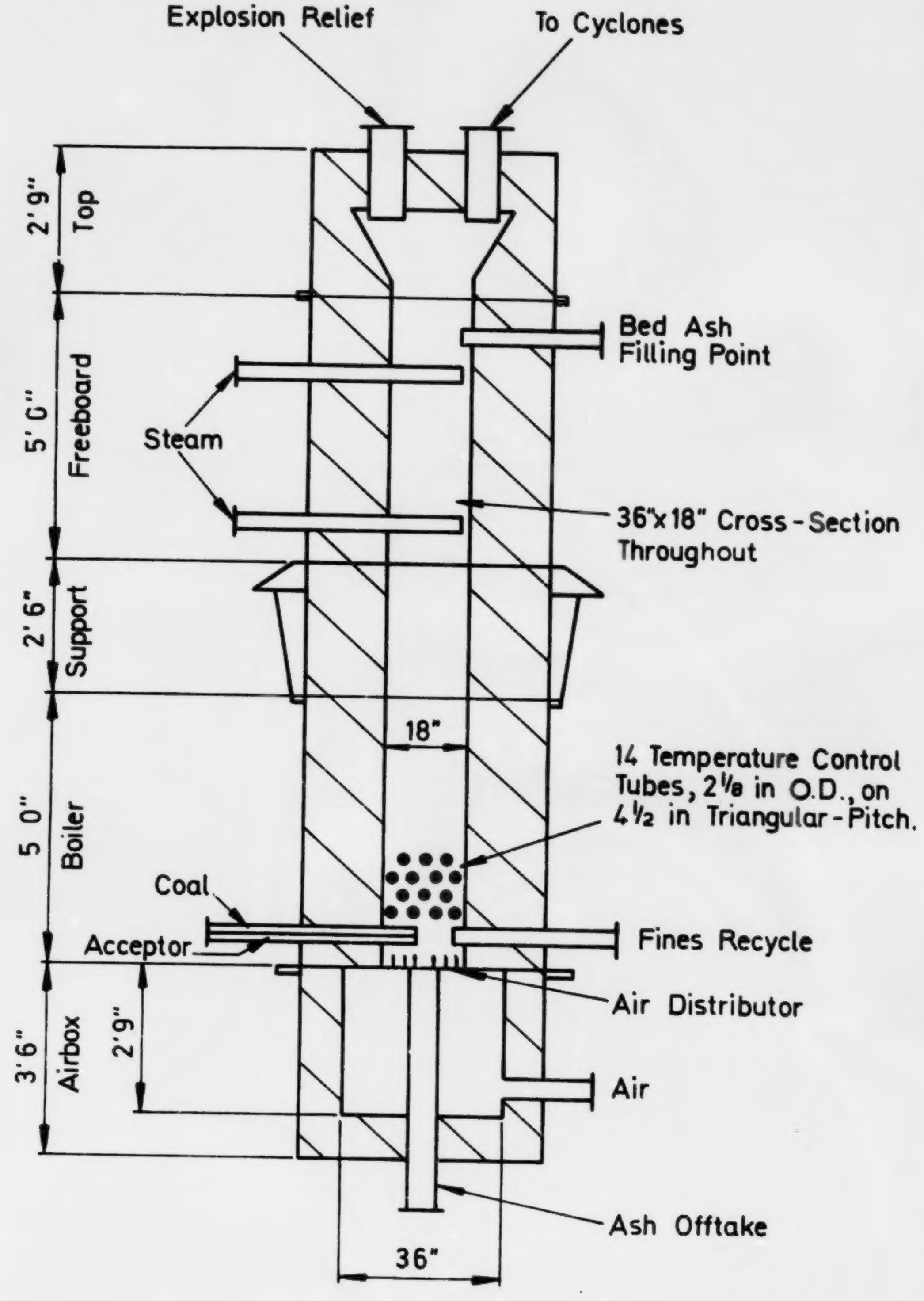

Explosion Relief
To Cyclones
2'9"
Top
5' 0"
Freeboard
Bed Ash Filling Point
Steam
36"x18" Cross-Section Throughout
2'6"
Support
18"
14 Temperature Control Tubes, 2 1/8 in O.D., on 4 1/2 in Triangular-Pitch.
5 0"
Boiler
Coal
Acceptor
Fines Recycle
Air Distributor
3'6"
Airbox
2'9"
Air
Ash Offtake
36"

Fig. 4.3 Task I. The 36in. combustor

of tests were carried out, as shown in Table 4.1. The plant was operated continuously for periods of up to 5 days separated by one or more weeks during which the coal and additive were prepared and the plant was checked. Test Series 1 required three periods of operation, designated Series 1.1, 1.2 and 1.3, but the remaining test series were each completed in a single operating period. Typical size distributions of the coals and additives as prepared are given in Table 4.2.

Table 4.2 Typical size distributions of prepared coals and additives

Material	Percentage in size range (sizes in μm)									Median μm
	+3175	+1680 -3175	+1003 -1680	+500 -1003	+250 -500	+125 -250	+66 -125	+45 -66	-45	
Pittsburgh coal, -⅛ in	0.3	17.7	17.1	22.6	15.0	9.5	7.7	3.5	6.6	648
Pittsburgh coal, -10 B.S.	0	0.2	11.9	34.4	21.2	12.9	8.8	3.1	7.5	456
Welbeck coal, -⅛ in	0	25.9	20.2	18.2	9.7	6.3	5.9	2.7	11.1	890
Limestone 18, -⅛ in	0	11.1	14.7	20.9	20.0	15.6	7.1	2.6	8.0	453
Limestone 18, -10 B.S.	0	0.1	5.9	15.1	22.0	23.5	12.2	5.0	17.2	207
Dolomite 1337, as rec'd.	0	14.9	28.1	30.3	8.9	4.2	5.7	2.3	5.6	874
Dolomite 1337, -10 B.S.	0	0.9	7.1	12.6	9.3	19.0	27.6	10.3	13.2	122
U.K. limestone, -⅛ in	0	11.1	13.9	16.3	22.7	14.2	8.2	2.9	10.7	391

4.2.3 Results

4.2.3.1 Pittsburgh coal and Limestone 18

Test Series 1, 2 and 5 were carried out using Pittsburgh coal and Limestone 18 without fines recycle. The results obtained are summarised in Tables 4.3 and 4.4

There was little difference in SO_2 reduction between the temperatures of 1470 and 1560°F and all data at these temperatures are shown in Fig. 4.4. Increasing fluidising velocity over the range 3 to 8 ft/s affected a substantial decrease in SO_2 reduction, but changing the limestone particle size had little if any effect. The SO_2 reduction fell by 30% when the temperature was decreased to 1380°F in Test 1.4.

Table 4.3 Summary of results obtained with Pittsburgh coal and Limestone 18, prepared to -1680 μm, without fines recycle (Task I)

Test No.	1.1	1.2	1.3	1.4	1.5	Datum‡	1.6	1.7	1.8	1.9	Datum‡	1.10	1.11
Fluidising velocity, ft/s	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	3.0	3.0	3.1
Bed temperature, °F	1470	1470	1470	1380	1560	1560	1560	1560	1560	1560	1470	1470	1470
Bed height, ft	2.3	2.2	2.2	2.2	2.2	2.2	2.2	2.1	2.2	2.1	2.3	2.3	2.1
Oxygen in off-gas, %	4.1	3.3	4.3	3.8	3.4	4.0	4.2	3.1	3.3	2.6	2.6	3.0	2.9
Unburnt carbon, %	7.8	9.2	7.2	7.8	6.2	-	7.6	7.9	7.9	8.5	-	8.2	6.7
Maximum freeboard temp, °F	1593	1562	1591	1567	1638*	-	1634	1648*	1652*	1657*	-	1582	1582
Ca/S mol ratio	0	0	2.2	2.2	2.2	0	1.3	2.2	3.3	1.2	0	2.2	3.3
SO_2, ppm	1750	2050	400	1020	360	2100	880	510	180	840	2020	330	42
S retention, %	9	18	83	56	85	-	61	78	93	65	-	86	97
SO_2 reduction, %	0	0	81	50	83	0	58	76	91	60	0	84	98
Cl^-, ppm	-	72	-	-	-	-	61	86	24	21	-	49	32
NH_3, ppm	-	3	-	-	-	-	0	6	2	0	-	2	2

* Limited by injection of steam

Based on a datum level of 2050 ppm

‡ Reference point - no limestone used.

Table 4.4 Summary of results obtained with Pittsburgh coal prepared to -3175 μm and Limestone 18 prepared to -3175 μm and -125 μm, without fines recycle (Task I)

Test No	Datum	2.1	2.2	2.3	Datum	2.4	2.5	Datum	5.1	5.2	5.3	5.4	5.5
Fluidising velocity, ft/s	8.1	8.1	8.1	8.0	4.0	4.0	3.0	4.0	4.0	8.0	7.8	8.0	8.0
Bed temperature, ^{o}F	1560	1560	1560	1560	1560	1560	1560	1560	1560	1560	1560	1560	1560
Bed height, ft	2.1	2.1	2.1	2.1	2.1	2.1	2.0	2.1	2.1	2.2	3.5	3.6	3.6
Oxygen in off-gas, %	2.2	2.9	2.9	2.5	3.0	3.2	2.6	-	3.2	3.2	2.4	2.8	3.0
Unburnt carbon, %	-	13.5	12.4	12.2	-	8.4	-	-	8.4	11.4	14.8	18.6	-
Maximum freeboard temp, ^{o}F	-	1634*	1634*	1634*	-	1688*	-	-	1627*	1603*	1600*	1596*	-
Maximum limestone size, μm	-	-3175	-3175	-3175	-	-125	-125	-	-3175	-3175	-3175	-3175	-3175
Ca/S mol ratio	0	1.1	2.3	2.9	0	1.0	1	0	1.7	1.6	1.9	5.7	6
SO_2 ppm	1830†	1200	900	650	2100†	1050	1050	2400†	850	1180	1040	80	11
S retention, %	-	44	62	73	-	54	-	-	67	55	62	97	-
SO_2 reduction,† %	0	34	56	68	0	49	49	0	65	51	57	97	100
NO_X, ppm	424	470	515	-	-	-	-	305	-	445	-	560	(550 (325
Cl^-, ppm	-	23	30	40	-	20	-	-	60	65	65	30	-
NH_3, ppm	-	4	4	0	-	0	-	-	2	4	2	3	-

* Limited by injection of steam.

† The sulphur content of the coal varied during these tests and the datum SO_2 concentration was estimated for each test from the coal's sulphur content, as follows:

Test 2.1	1830 ppm
Tests 2.2 to 2.5	2050 ppm
Tests 5.1 to 5.5	2400 ppm

† Reference point — no limestone used.

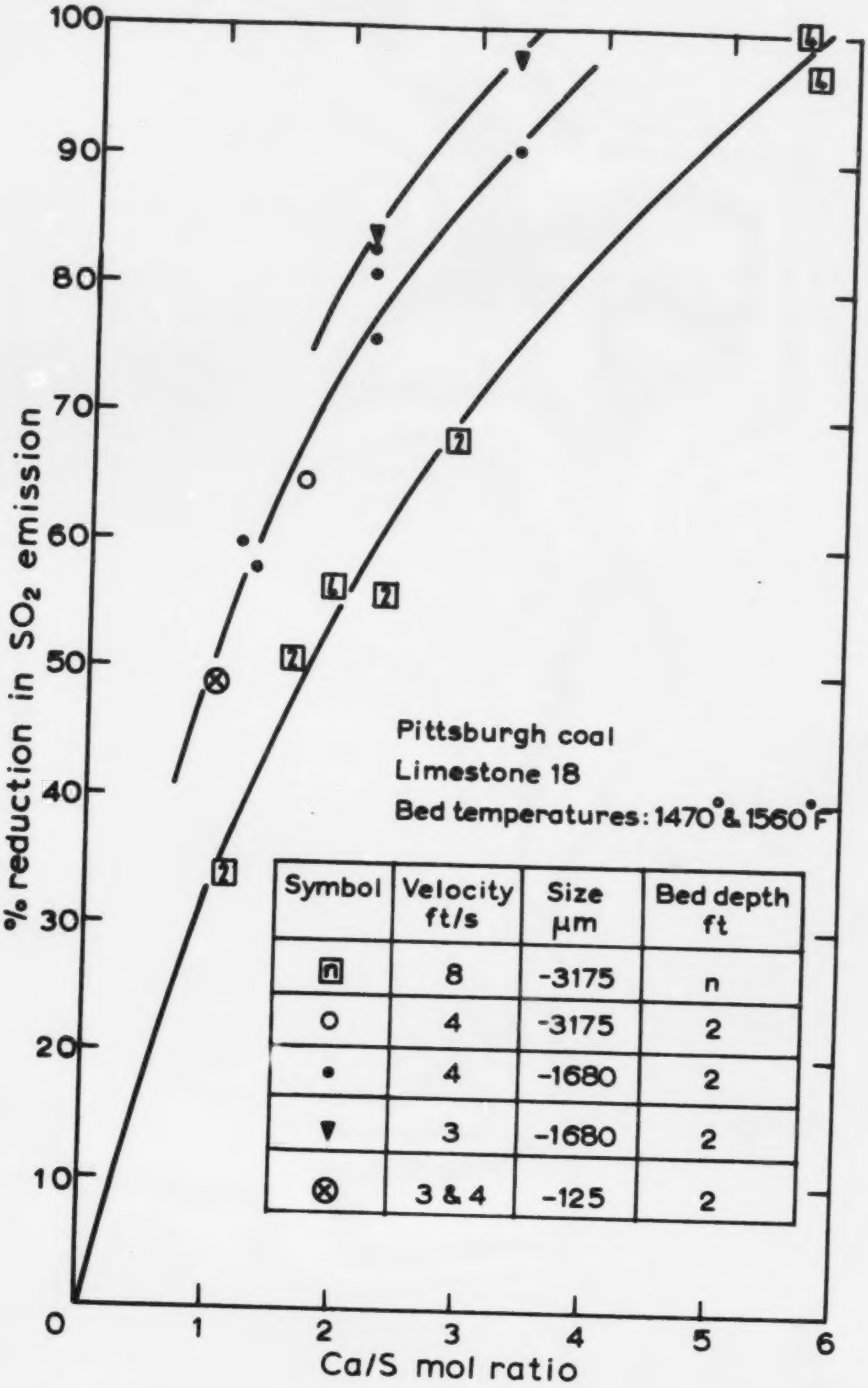


Fig. 4.4. Task I. SO_2 reduction in the 36 in. combustor for Limestone 18 and Pittsburgh coal. 1470-1560°F

In these tests the concentrations of CO and CH_4 were below the minimum level of detection of 200 ppm. At 4 ft/s the bed temperature was uniform to ± 10°F, but there was a tendency for the maximum temperature to occur above the coal feed point. At 8 ft/s with a 2 ft deep bed there was a hot spot above the coal feed, about 60°F above the mean bed temperature. This did not occur in the deeper beds used in Test Series 5. A high proportion of the limestone was elutriated from the bed; about 80% at 4 ft/s and 90% at 8 ft/s.

Gas samples taken 2 ft above the bed in Test 1.1 and in Test Series 5 showed a marked radial distribution of SO_2 concentrations, as shown in Table 4.5.

Table 4.5 Variation in SO_2 concentration 2 ft above the bed

Test No.	SO_2 concentration, p p m				
	Above feed	3 in radius	6 in radius	12 in radius	Stack
1.1	2800	-	1750	1400	1750
Series 5 datum	2350	1950	1250	-	2400
5.1	1300	-	400	-	850
5.2	2150	-	1400	-	1180

4.2.3.2 Pittsburgh coal and Dolomite 1337

Test Series 4 and 6 were carried out using Pittsburgh coal and Dolomite 1337. The tests were carried out without fines recycle, except for a single experiment, Test 4.6, which was carried out in order to allow comparison with the pressurised combustor, Task II. The results obtained are summarised in Table 4.6.

As with Limestone 18 there was little difference between SO_2 reductions obtained at 1470 and 1560°F. However, in contrast to limestone, there was no decrease in reduction when the temperature was reduced to 1380°F in Test 4.2 (cf Tests 4.3 and 4.4). All the data obtained at the three temperatures are shown in Fig. 4.5. As with limestone, increasing the fluidising velocity caused a substantial decrease in SO_2 reduction. At 8 ft/s, and a Ca/S mol ratio of 5, increasing the bed height from 2 to 7 ft appeared to give a small improvement in the already high SO_2 reduction.

Table 4.6 Summary of results obtained with Pittsburgh coal and Dolomite 1337 (Task I)

Test No.	Datum	4.1	4.2	4.3	4.4	4.5	4.6++	Datum	6.1	6.2	6.3	6.4	6.5
Fluidising velocity, ft/s	4.0	4.0	4.1	3.8	4.0	2.1	2.2	8.0	8.0	8.0	8.1	8.0	8.0
Bed temperature, °F	1470	1470	1380	1560	1470	1470	1470	1560	1560	1560	1560	1560	1560
Bed height, ft	2.1	2.1	2.1	2.1	2.1	3.7	3.8	2.7	2.7	2.7	4.0	7	5.5
Maximum coal size, μm	1680	1680	1680	1680	1680	1680	1680	3175	3175	3175	3175	3175	3175
Oxygen in off-gas, %	2.5	3.0	3.7	2.9	3.8	2.8	3.1	2.9	3.0	3.3	3.4	2.7	3.0
Unburnt carbon, %	-	9.1	8.0	10.5	9.0	8.0	0.7		12.9	12.9	15.0	15.5	15.6
Maximum freeboard temp, °F	-	1591	1530	1560*	1594	1510	1522	-	1648*	1638*	1629	1620	1636
Maximum dolomite size, μm	-	1680	1680	1680	1680	1680	1680	-	3175	3175	3175	3175	3175
Ca/S mol ratio	0	3.1	2.6	2.7	2.7	2.2	1.6	0	2.5	5.4	5.3	5.2	5.0
SO_2, ppm	2240	380	620	600	580	380	20	2190	840	280	260	155	280
S retention, %	-	85	75	76	75	86	99	-	67	88	90	94	89
SO_2 reduction, %	0	83	72	73	74	83	99	0	6	87	88	93	87
NO_x, ppm	-	234	-	244	-	360	392	390	-	390	360	400	425
Cl^-, ppm	-	46	44	54	42	29	38	-	62	59	59	55	60
NH_3, ppm	-	34	6	6	6	7	8	-	4	9	15	7	12

++ With fines recycle at about five times the coal feed rate.

* Limited by injection of steam.

' Based on datum level of 2240 ppm.

· Based on datum level of 2190 ppm.

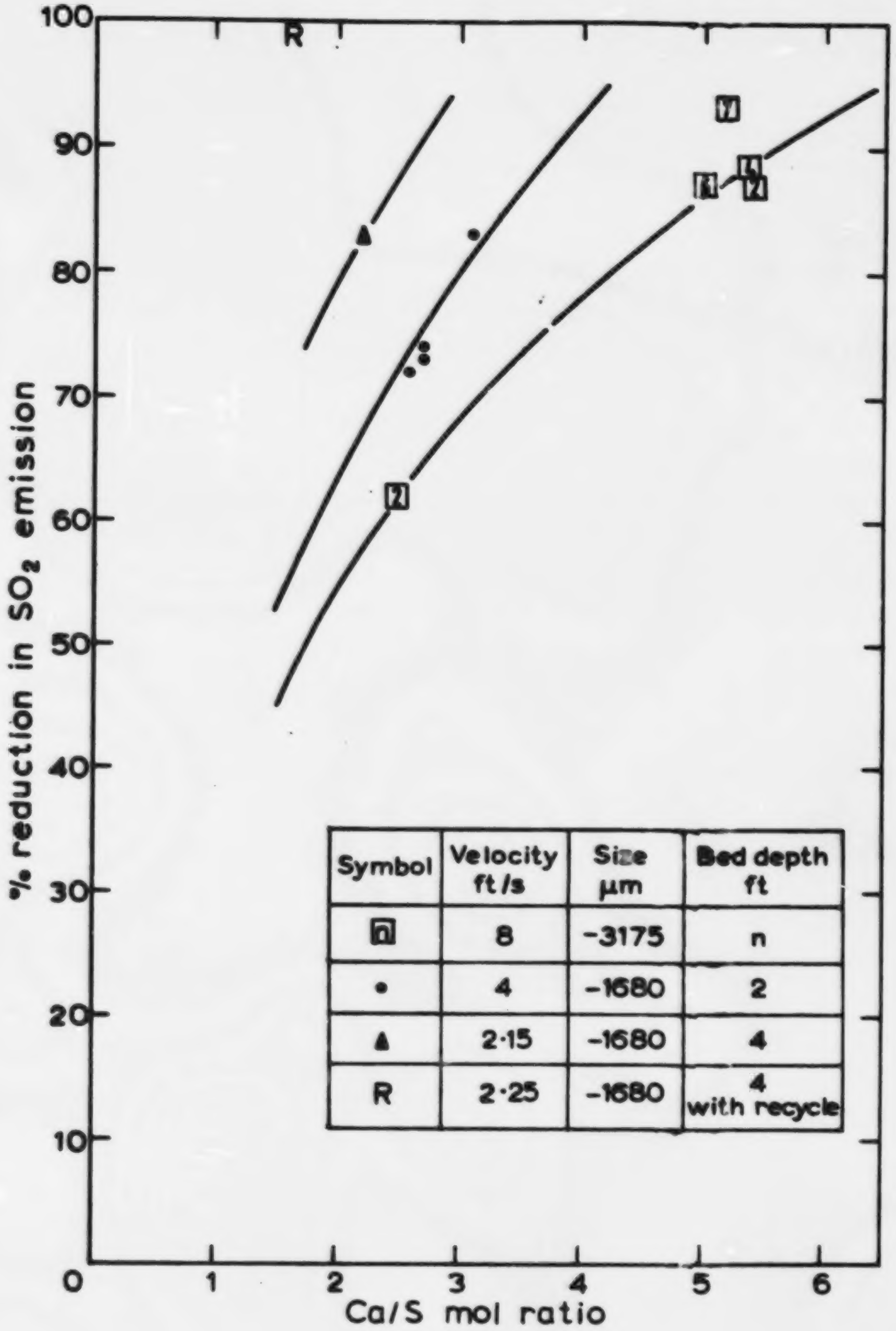


Fig. 4.5 Task I SO_2 reduction in the 36 in. combustor for Dolomite 1337 and Pittsburgh coal. 1380-1560 °F

Table 4.7 Summary of results obtained with Welbeck coal and U.K. limestone prepared to -3175 μm, without fines recycle (Task I)

Test No.	3.1	3.2	3.3	3.4	3.5	3.6
Fluidising velocity, ft/s	7.9	8.0	8.0	7.9	8.0	4.1
Bed temperature, ^{o}F	1560	1560	1560	1560	1560	1560
Bed height, ft	2.1	2.1	2.1	2.2	3.8	2.3
Oxygen in off-gas, %	2.9	3.0	3.4	3.4	3.3	3.1
Unburnt carbon, %	10.9	9.7	9.2	11.9	12.3	6.2
Maximum freeboard, ^{o}F	1650*	1636*	1648*	1647*	1611*	1656*
Ca/S mol ratio	0	1.8	2.1	2.8	2.8	3.0
SO_2 by iodine, ppm	1480	910	740	540	540	420
S retention, %	14	45	53	65	68	73
SO_2 reduction[+] %	0	38	50	64	64	72
Cl^-, ppm	430	565	455	380	455	410
NH_3, ppm	11	8.5	8	11.5	13	10

* Limited by injection of steam.

[+] Based on datum level of 1480 ppm.

Fines recycle at 2 ft/s resulted in a dramatic reduction in SO_2 emission to only 20 ppm at a Ca/S mol ratio of 1.6.

The effect of bed temperature on SO_2 reduction was investigated by varying the bed temperature over the range 1420 to 1620°F while maintaining all other operating conditions as in Test 6.3. The SO_2 concentration indicated by the infra-red analyser responded almost immediately to changing temperatures and the variation of SO_2 reduction with temperature is shown in Fig. 7.7

The fines recycle rate in Test 4.6 was about five times the coal feed rate. The CO and CH_4 concentrations in the off-gas were, as before, below the minimum level of detection of 200 ppm. The bed temperature was uniform to within about ± 10°F at a fluidising velocity of 4 ft/s and within ± 20°F at 8 ft/s. Over 90% of the dolomite feed was elutriated from the bed at all operating conditions other than with fines recycle. Even with recycle at a fluidising velocity of 2 ft/s, about 80% of the dolomite eventually passed through the primary cyclone. It was not possible to maintain a bed of more than 6 ft deep, even when feeding coarse dolomite at a Ca/S ratio of five.

4.2.3.3 Welbeck coal and U.K. limestone

Test Series 3 was carried out using Welbeck coal and U.K. limestone prepared to minus ⅛ in, (-3175 μm). The effect of the Ca/S ratio and bed height were investigated at 8 ft/s and a single test was carried out at 4 ft/s. The results of these tests, which were all without fines recycle, are summarised in Table 4.7.

The effect of bed temperature was investigated by varying it over the range 1470 to 1630°F during a period of two hours and monitoring the SO_2 emission using the infra-red analyser. As with dolomite, the response to changing temperature was almost instantaneous, (Fig. 7.23). The SO_2 reduction obtained is plotted against the bed temperature in Fig. 7.7.

The bed temperature was uniform to within ± 20°F and there was no 'hot spot' above the coal feed point. About 80% of the limestone was elutriated from the bed at 4 ft/s, and about 90% at 8 ft/s. NO_x measurements were not made during these tests. The CO and CH_4 concentrations were again below the minimum level of detection of 200 ppm.

4.3 The 48 x 24 in Pressurised Combustor (Task II)

The work carried out on the pressurised combustor is described in detail in Appendix II.

4.3.1 Description of the plant

A flow diagram of the pressurised combustor plant is shown in Fig. 4.6 and details of the combustor are given in Fig. 4.7. The combustion vessel was a refractory-lined shaft of approximately 48 x 24 in cross-section, 10 ft high, housed in a cylindrical steel shell, 22 ft long x 6 ft i.d. having domed ends and capable of withstanding an internal pressure of up to 100 psig. The walls of the combustor were designed to withstand a pressure differential of about ± 5 psi.

The air distributor plate was fitted with 465 bubble caps on a 1½ in square pitch, each containing four horizontal jets, 1 in above the distributor plate. Combustion air, preheated to 400-500°F, was supplied, via a plenum chamber, through the distributor plate. Combustion was initiated by preheated combustion air derived from three gas burners located in the plenum chamber. After coal combustion was established, the gas burners were isolated.

The coal and additive were premixed and fed via a pressurised hopper system to four pneumatic feed lines, each of which terminated in a nozzle that protruded 4 in into the bed. The nozzles were located 12 in from each end of both of the 48 in walls. Heat transfer tubes were immersed in the bed on a staggered pattern of 18 rows of 7 or 8 tubes per row, with horizontal and vertical pitches of approximately 6 in and 1½ in respectively. Twelve of the tubes were air-cooled, six preheating the combustion air and six forming corrosion specimen assemblies. The corrosion specimen assemblies were similar to those described in section 4.1. The majority of the remaining 53 tubes could be used as water-cooling circuits, the remainder being dummies. The bed temperature was controlled by varying the number of water-cooling circuits in use.

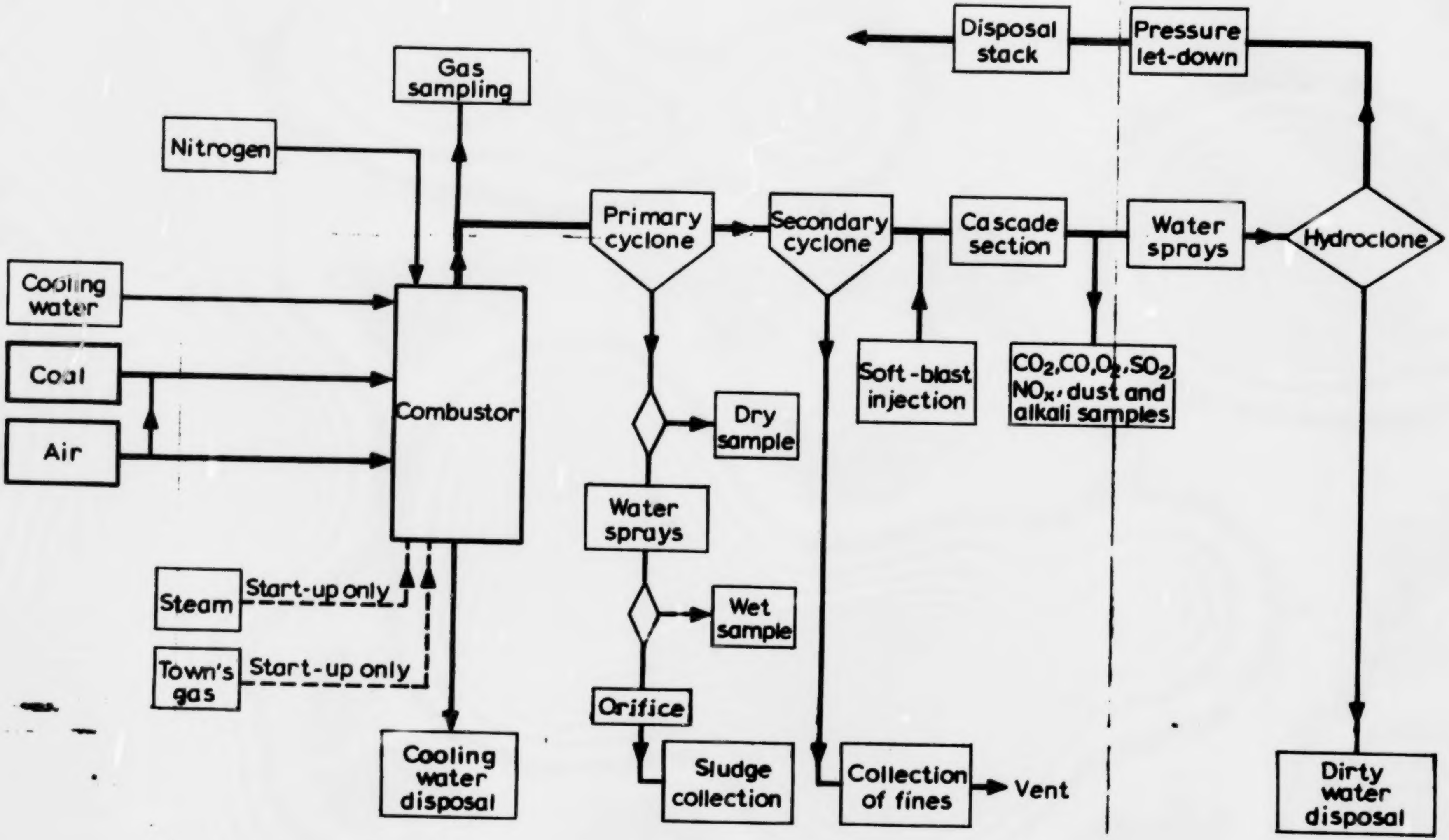

Disposal stack
Pressure let-down
Gas sampling
Nitrogen
Primary cyclone
Secondary cyclone
Cascade section
Water sprays
Hydroclone
Cooling water
Coal
Air
Combustor
Soft-blast injection
CO_2,CO,O_2,SO_2 NO_x, dust and alkali samples
Dry sample
Water sprays
Steam
Start-up only
Wet sample
Town's gas
Start-up only
Orifice
Cooling water disposal
Sludge collection
Collection of fines
Vent
Dirty water disposal

Fig 4.6 Task II. Flow diagram of 48in x 24 in pressurised combustor plant

NOTES ON THE DIAGRAM OF THE 48 in x 24 in PRESSURISED COMBUSTOR

1. Water supply to water-cooled circuits
2. First-stage dust-collecting cyclone
3. Internal recirculation cyclone
4. Balance air supply
5. Gas burners for start-up
6. Bed removal pipe
7. Pressure shell
8. Cooled liner
9. Combustor casing
10. Second-stage dust-collecting cyclone
11. Air supplies to air preheating tubes and corrosion assemblies
12. Cascade housing
13. Sampling point for alkali content of gases
14. Mixing baffle
15. Sampling point for NO_x gases
16. Spray nozzles
17. Deposition probe (Not used in the APCO programme).
18. Dust sampling and O_2, CO_2, CO, probe
19. Exhaust to pressure let-down valve
20. Dip-leg from recirculation cyclone

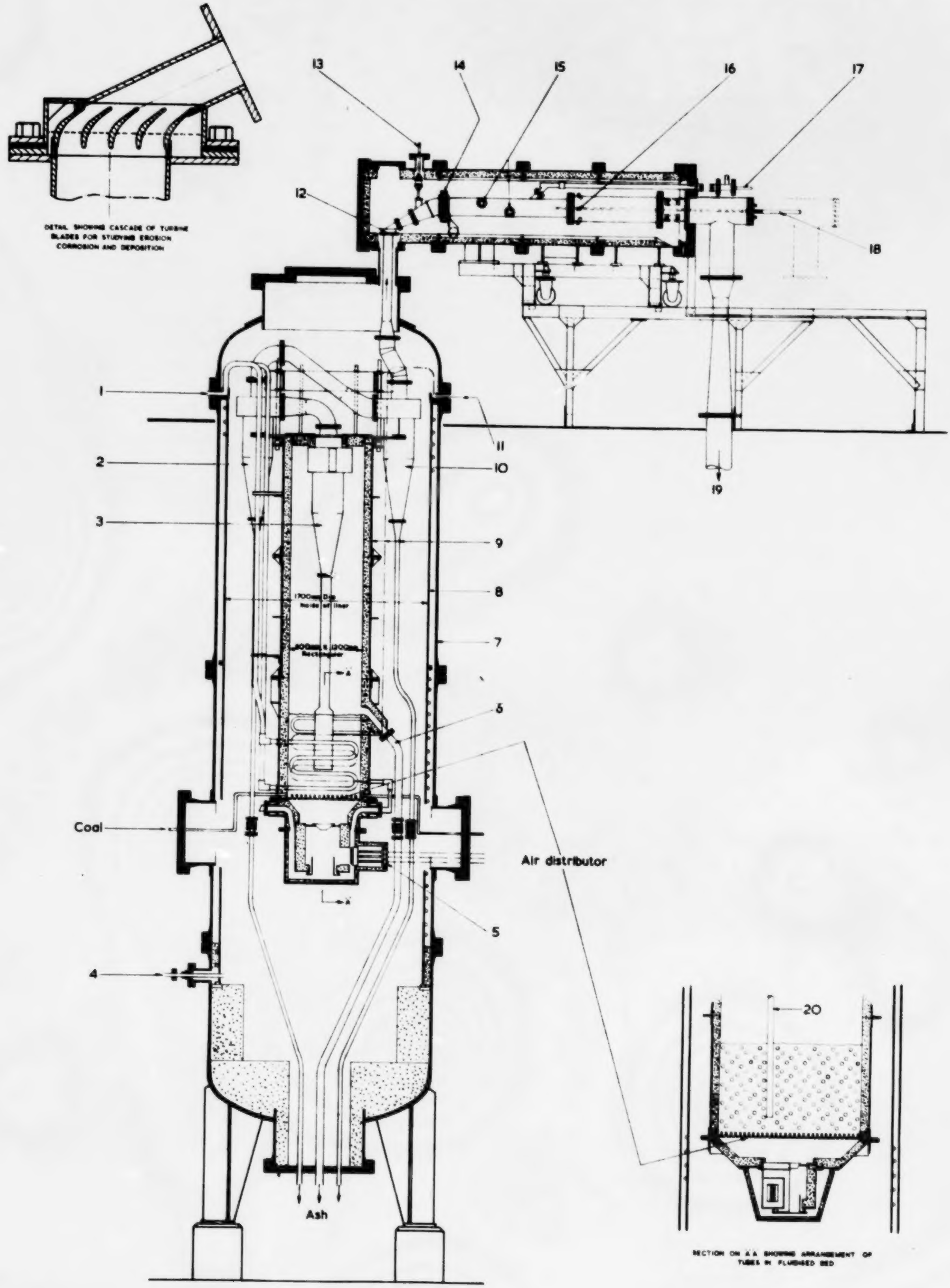

DETAIL SHOWING CASCADE OF TURBINE BLADES FOR STUDYING EROSION CORROSION AND DEPOSITION
13
14
15
16
17
12
18
1
11
2
10
19
3
9
1700mm Dia. Inside of liner
8
600mm x 1200mm Rectangular
7
A
6
Coal
Air distributor
A
5
4
20
Ash
SECTION ON A.A SHOWING ARRANGEMENT OF TUBES IN FLUIDISED BED

Fig 4.7 Task II. The 48in x 24in pressurised combustor

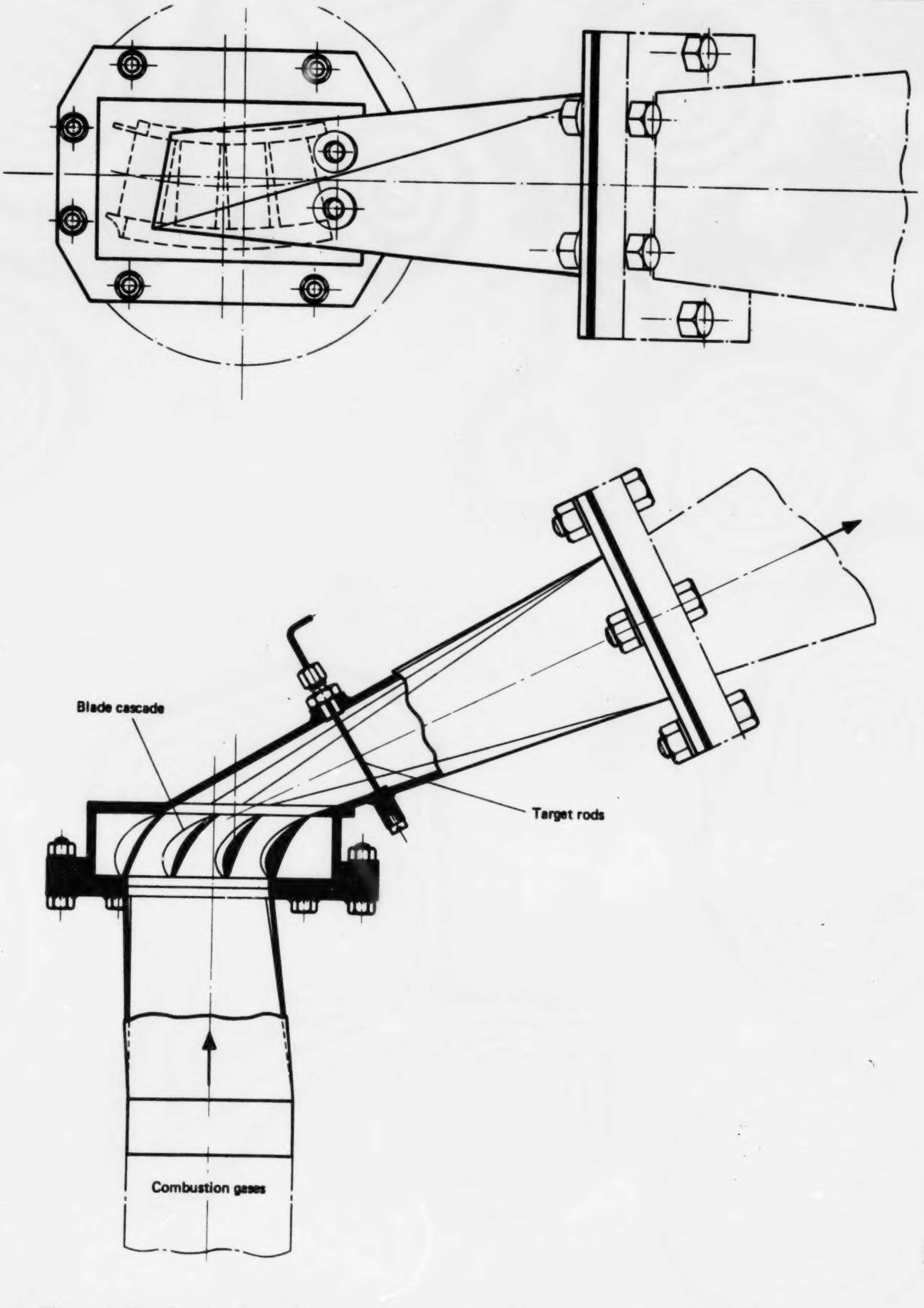

Blade cascade
Target rods
Combustion gases

Fig. 4.8 Task II. Arrangement of blade cascade and target rods

A bank of four rows of uncooled tubes, on a nominal 3 in triangular pitch, was located immediately above the bed to act as a horizontal baffle.

Water-cooled circuits were provided in the freeboard zone to limit the exit gas temperature to 1500°F.

The waste gases passed through a 10 in diameter internal recirculation cyclone with a dip-leg passing back into the bed. The amount of material being recycled back to the bed was unknown, but available evidence suggests that it was small and the system probably behaved as a non-recycle system. Subsequently the partially-cleaned gases passed through two 10 in diameter cyclones arranged in series from which collected fines were removed continuously by positive blowdown systems. The cleaned gases were then accelerated through a gas turbine blade cascade, (Fig. 4.8) quenched and cleaned in a venturi scrubber and hydroclone before being exhausted to the stack via a pressure let-down valve.

The main gas sampling point was immediately after the cascade. CO, CO_2 and CH_4 were continuously monitored on infra-red analysers and O_2 on a paramagnetic analyser. SO_2 was determined by bubbling through iodine and in the later tests was also continuously monitored using a Hartmann Braun infra-red analyser. NO_X was measured using both the Saltzman method and the BCURA NO_X box. All the outlet solid streams were sampled and the bed level was maintained at the required level by periodically extracting material directly from the bed.

4.3.2 Experimental programme

Tests were carried out using Pittsburgh coal with Dolomite 1337 and Limestone 18, and using Welbeck coal with U.K. limestone. Five series of tests were carried out, as shown in Table 4.1. The plant was operated continuously for periods of up to 4 days separated by one or more weeks during which the coal and additive were prepared and the plant was checked. Size distributions of the coals and additives are given in Table 4.8

Table 4.8 Typical Size Distributions of Prepared Coals and Additives (Task II)

Material	Percentage in size range (size in μm)							Median size μm
	+1588	-1588 + 794	-794 +500	-500 +211	-211 +152	-152 +75	-75	
Welbeck coal	0	14.4	21.7	41.7	4.8	5.9	11.5	400
Pittsburgh coal	0	21.2	17.4	22.1	12.5	12.4	14.4	360
Dolomite 1337 (Tests 2 and 3)	0	75.5	17.8	2.4	0.9	1.2	2.2	1100
Dolomite 1337 (Tests 4 and 5)	0	27.8	17.5	13.3	8.5	12.6	20.3	400
Limestone 18	0	16	15	2.1	18	10	20	270

Fluidising velocity, bed depth and bed temperature were maintained substantially constant throughout the programme at nominal values of 2 ft/s, 3.75 ft and 1470°F respectively. Operating pressure was either 3.5 or 5 atm absolute.

The test conditions were largely predetermined by the coal/additive mixture prepared before a test. Measurements were made continuously throughout a test series and test periods were selected in retrospect to coincide with periods when the SO_2 emission had reached equilibrium. The duration of these test periods was from 4½ to 31 hours.

4.3.3 Results

The main results are tabulated in Table 4.9 and the data on the reduction of SO_2 emission are plotted in Fig. 4.9. The main conclusions, as far as Task II is concerned are:

(1) Reduction of SO_2 emission was not affected by pressure in the range 3½ to 5 atm.

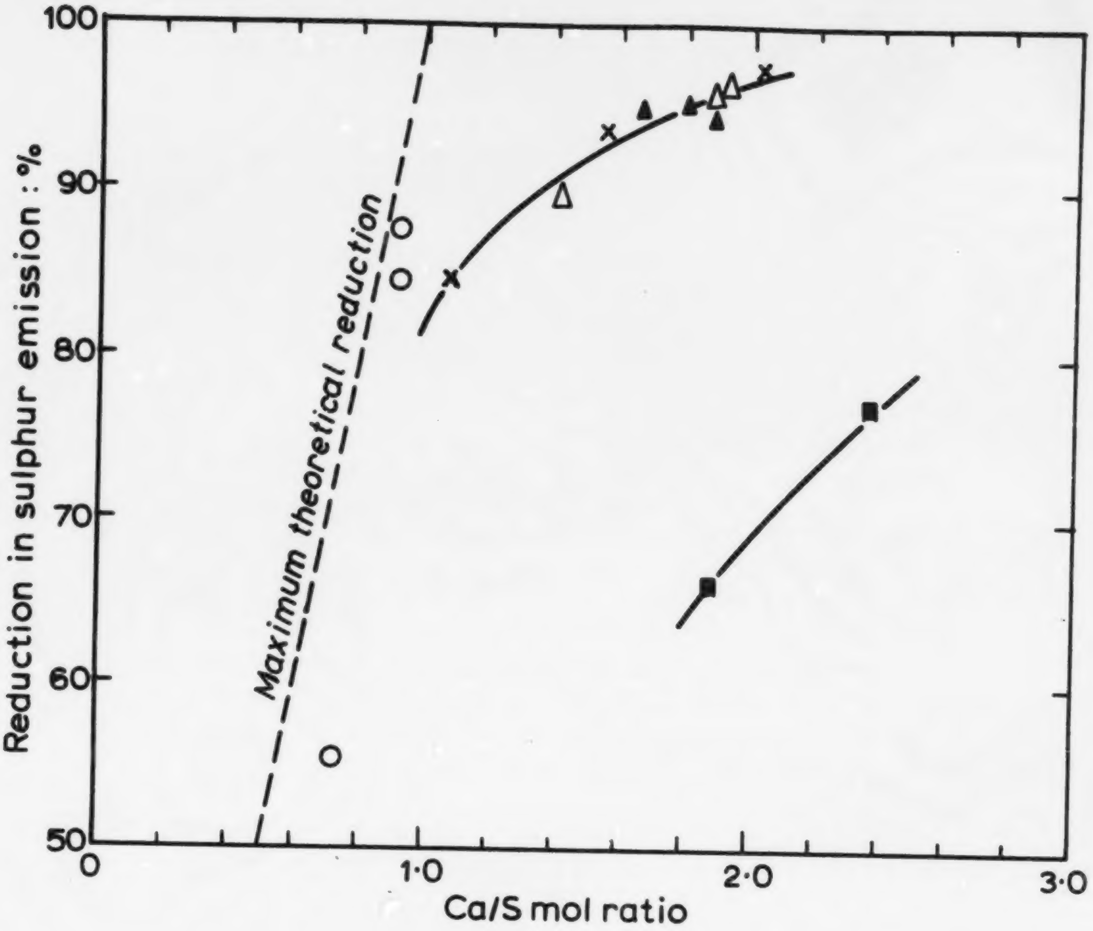
(2) Altering the median size of the additive (in this case Dolomite 1337) from 1100 to 400 micron did not affect the reduction in SO_2 emission. The change in size was produced by widening the size distribution, i.e., by increasing the proportion of fines.

Table 4.9. Summary of results obtained on 48 in x 24 in pressurised combustor (Task II)

Fluidising velocity: 2.0 ft/s
Bed temperature: 1470°F
Bed depth: 3.75 ft
Top size of coal & additive: 1588 μm (1/16 in)

Test	1.1	1.2	1.3	1.4	1.5	2.1	2.2	2.3	2.4	3.1	3.2	4.1	4.2	5.1	5.2	5.3
Coal Additive	Welbeck U.K. Dolomite					Pittsburgh Dolomite 1337				Pittsburgh Dolomite 1337		Pittsburgh Dolomite 1337		Pittsburgh Limestone 18		Dol. 1337
Duration of test period h	4½	12	27½	14½	26	13½	21	29	4½	11	8	25½	31	23	16	8
Pressure	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5	5	5	5	5	5	5	5	5
O_2 in exhaust %	3.8	4.2	4.6	5.1	4.8	3.0	4.5	4.9	6.3	5.3	5.1	5.8	5.3	3.6	3.8	5.3
Carbon loss %	3.1	2.9	2.2	2.2	1.4	2.9	3.0	3.9	2.7	1.8	1.1	0.9	1.3	1.2	0.5	0.8
Median size of additive μm	750					1100				1100		400		270		400
Ca/S mol ratio	0	0.77	0.73	0.91	0.92	1.41	1.88	1.93	1.88	1.65	1.80	1.54	2.02	1.87	2.38	1.08
SO_2 in exhaust ppm	1020	620	430	100	150	210	90	70	110	100	100	130	50	690	470	310
Sulphur retention %	9	52	62	90	86	92	96	97	95	95	95	94	98	67	79	85
SO_2 reduction %	0	39	57	89	85	89	96	96	95	95	95	94	98	66	77	85
SO_3 in exhaust ppm	9	14	14	8	5	1	0	1	-	-	-	-	-	-	-	-
NO_x in exhaust ppm	40	-	80	120	130	80	130	90	100	160	-	140	190	90	90	140
Cl^- in exhaust ppm	490	590	640	460	330	80	70	50	-	-	-	40	40	30	50	50
Na in exhaust (gas) ppm	1.1	0.9	0.7	0.4	0.4	0.7	0.4	0.2	-	-	-	1.1	1.1	1.6	2.7	0.7
K in exhaust (gas) ppm	0.3	0.2	0.2	0.2	0.2	0.2	0.2	0.1	-	-	-	0.3	0.4	0.7	0.9	0.2

Note: Equilibrium SO_2 emission may not have been reached in Test 1.2.



Fluidising velocity : c 2ft/s
Bed depth : 3·75ft
Bed temperature : c1470°F

Coal	Acceptor		Pressure : atm. abs.	
	Type	Median size: micron	$3\frac{1}{2}$	5
Welbeck	U.K. Dolomite	750	○	
Pittsburg	Dolomite 1337	1100	△	▲
Pittsburg	Dolomite 1337	400		×
Pittsburg	Limestone 18	270		■

Fig. 4.9 Task II. Reduction of sulphur emission in the pressurised combustor

(3) The percentage SO_2 reduction with Welbeck/U.K. dolomite appeared to be slightly higher than with Pittsburgh/Dolomite 1337, although the range of Ca/S ratios investigated did not overlap sufficiently for a firm conclusion to be drawn.

(4) Reductions obtained with Limestone 18, although considerably lower than with dolomite (on a Ca/S basis), were surprisingly high in view of the fact that limestone does not calcine at these conditions.

The time taken to reach an equilibrium SO_2 emission was substantial when dolomite was the additive - about 20 to 50 hours when the initial bed contained no dolomite. The approach to steady state is discussed further in Section 7.1.12.

e major loss of combustion efficiency in all tests was in the carbon of size less than 50 micron elutriated from the bed.

Combustion in the freeboard, based on heat balance between the top of the bed and the top of the freeboard, amounted to 2 to 3% of the coal heat input.

The temperature of the bed showed a small, but consistent, rise of 30 to 40°F between a level near the bottom of the bed and one near the top. At any particular level the variation in temperature was about ± 20°F, although no measurements near a coal feed point were made.

The dust burden of the gases passing over the cascade was about 150 lb dust/10^6 lb gas (about 0.1 gr/scf) when burning Pittsburgh coal. This was about twice the dust loading obtained when burning Welbeck coal. The inert input was considerably higher with Pittsburgh coal, partly because of its higher S content, and partly because of the higher Ca/S ratios generally used with the Pittsburgh coal.

The dust was sized by Coulter count and found generally to have a median size of 6 to 8 micron with about 90% less than 30 micron. As with all determinations of size distributions of this order, however, the value of the data, particularly from the point of view of turbine erosion, is open to question. Earlier tests with Welbeck coal had shown that most of the larger dust particles were in the shape of 'platelets' which would not be regarded as erosive. The accuracy of the Coulter counter technique for this type of particle is open to doubt.

The cascade blades were not cleaned between tests and the appearance did not vary greatly from test to test. Usually there was a light accumulation of dust on the leading edge with flecks of dust adhering to the concave faces and negligible deposition on the convex faces. There were no signs of sintered deposits or of erosion. Photographs of the cascade blades are given in Appendix 2.

The target rods usually had a small knife-edge of deposit on their leading face, and had developed a considerable 'tail'. Cross-sectioning and examination under a microscope revealed no evidence of corrosion or erosion.

The data obtained on corrosion of tubes in the bed is given in section 4.7, together with data from other pilot plants.

4.4 The 27 in Combustor (Task III)

The work carried out on the 27 in combustor is described in detail in Appendix III.

It was originally intended that only corrosion investigations would be made on this plant, but subsequently the objectives of the work were extended to include investigations into sulphur emission and when possible, nitrogen oxides emission.

4.4.1 Description of the plant

A flow diagram of the 27 in combustor plant is shown in Fig. 4.10 and a section through the combustor in Fig. 4.11. The cylindrical section containing the fluid-bed was 27 in diameter and the shaft above this section diverged to 46 in diameter for the lower 2 ft of the freeboard before returning to a cylindrical section 24 in diameter. The height of the bed zone was 2 ft and the total height of the freeboard was 11 ft. The walls of the bed zone and freeboard consisted of twenty

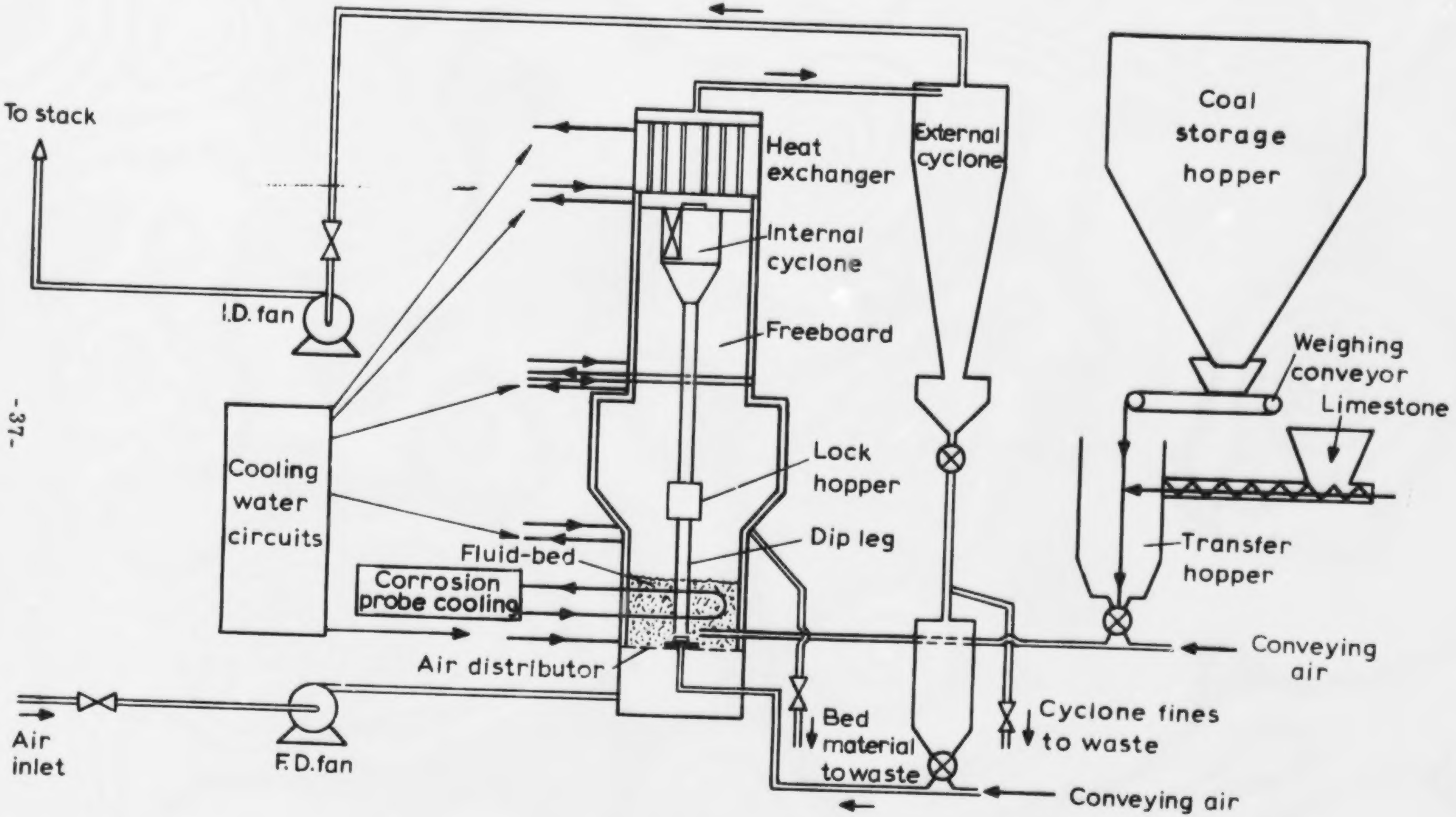

To stack
I.D. fan
Cooling water circuits
Corrosion probe cooling
Air inlet
F.D. fan
Heat exchanger
Internal cyclone
Freeboard
Lock hopper
Dip leg
Fluid-bed
Air distributor
Bed material to waste
External cyclone
Cyclone fines to waste
Conveying air
Conveying air
Coal storage hopper
Weighing conveyor
Limestone
Transfer hopper

Fig. 4.10 Task III. Flow diagram of 27in. combustor plant

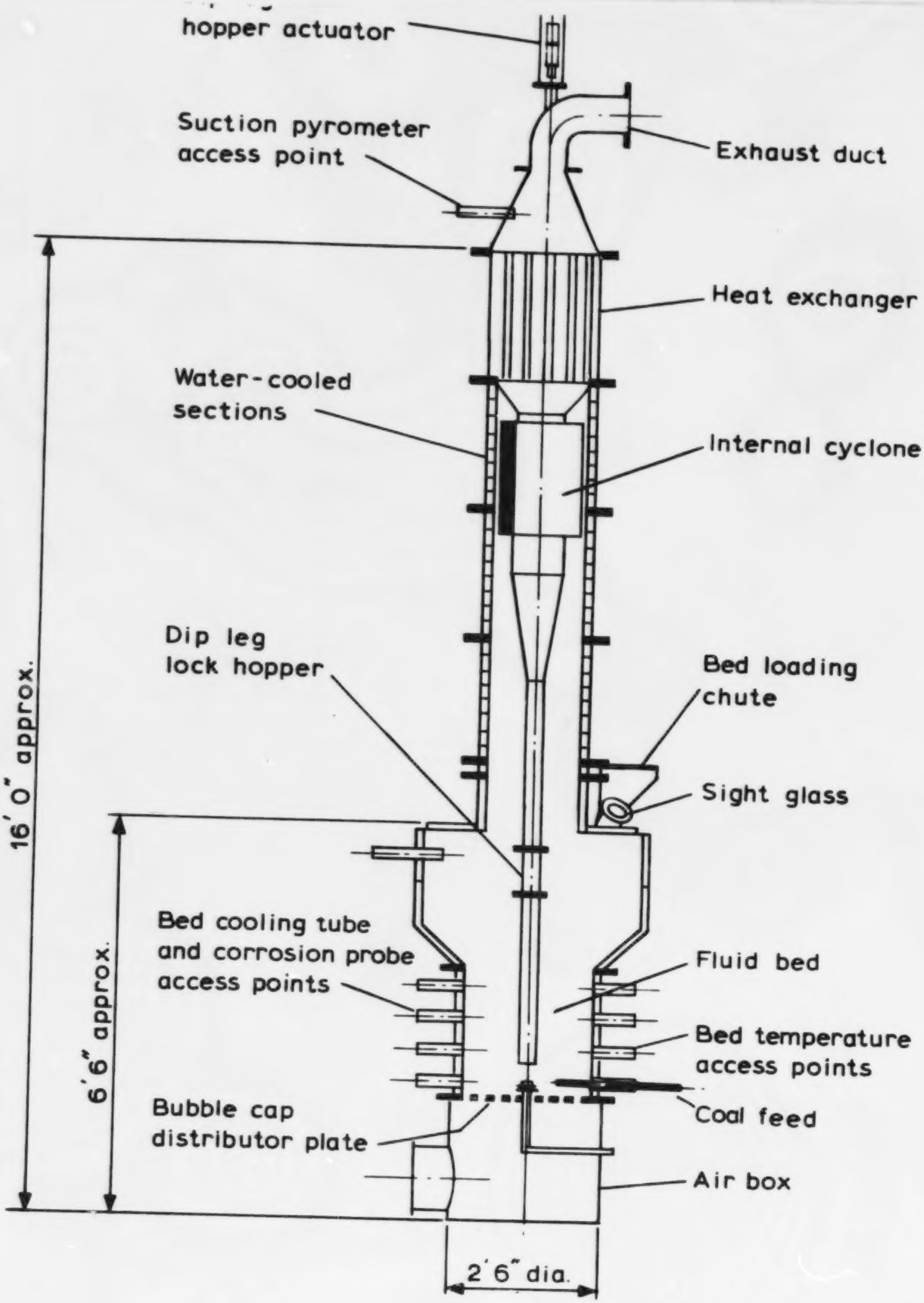

hopper actuator
Suction pyrometer access point
Exhaust duct
Heat exchanger
Water-cooled sections
Internal cyclone
Dip leg lock hopper
Bed loading chute
Sight glass
16' 0" approx.
6' 6" approx.
Bed cooling tube and corrosion probe access points
Fluid bed
Bed temperature access points
Coal feed
Bubble cap distributor plate
Air box
2' 6" dia.

Fig. 4.11 Task III. The 27in combustor

water-cooled jackets. Combustion products leaving the freeboard passed into a vertical water-cooled heat exchanger before entering the external dust cleaning cyclone.

The bed was supported on a bubble cap distributor plate, air for combustion being supplied via a plenum chamber located directly below the distributor plate. Crushed coal and additive were metered into a hopper, transported pneumatically to the combustor and injected into the fluid-bed via a 'Y' feeder. The two 1 in diameter arms of the 'Y' formed injection points which were radially equidistant from the axis of the combustor at a distance apart of 0.3 ft approximately.

A "mushroom" gasburner fitted in the centre of the distributor plate supplied towns gas for start up. During normal operation it was used to distribute fines recycled from the external cyclone.

A low efficiency cyclone positioned in the freeboard recycled +50 micron particles to the bed via a dip-leg and lock-hopper system, whilst a high efficiency cyclone external to the combustor removed solids greater than 10 micron from the combustion products. A controlled portion of the fines collected by the external cyclone could be recycled pneumatically to the bed via the "mushroom" burner and the remainder was discharged to collection drums.

Access ports for bed cooling tubes, corrosion tube assemblies and other probes were provided in the walls of the bed section. The 2 in diameter tubes were arranged at 5 in centres horizontally and 6⅞ in centres vertically: the dip leg from the internal cyclone prevented the use of intermediate tubes to form a triangular pattern: the tubes were cooled with either steam or air. Four corrosion tubes were used for the first two test series. Higher bed temperatures were required for the third series and only two tubes were used.to reduce the cooling load on the bed.

The iodine method was the main technique used for determining the SO_2 concentration in the gases, but an infra-red analyser was also used from Test Series 2 onwards. NO_X was determined using Saltzman's method and the BCURA NO_X box.

4.4.2 Experimental programme

Four series of tests were carried out at atmospheric pressure using -3175 micron Pittsburgh coal. The main operating conditions of these tests are detailed in Table 4.1. Two different American acceptors were used, Limestone 18 and Dolomite 1337, the former being examined at two levels of particle size.

The plant was run continuously for 100,500 or 1000 hours, each run period being separated by several weeks for refurbishing and checking the plant plus preparation of coal and additive. Test Series 1 was run at constant conditions throughout, whereas the remaining three test series were sub-divided into periods having different operating conditions. The actual test periods in Test Series 2 and 3 were normally of 16 hours duration, preceded by a settling down period of minimum duration of 18 hours. In Test Series 4, which ran for 100 hours only, the settling down period for the tests was 6 hours and the actual test period was 4 hours.

4.4.3 Results

Test Series 1 was a 500 h corrosion test carried out under constant operating conditions without limestone addition. The corrosion data obtained in this and subsequent test series are given in section 4.7, together with corrosion data from other pilot plants. Other results obtained are given in Table 4.10.

Test Series 2 was primarily a 1000 h corrosion test with addition of Limestone 18 and was carried out under approximately constant combustion conditions. However two sizes of limestone, minus 3175 and minus 150 microns, were used over a wide range of Ca/S mol ratios, both with and without recycle of fines from the external cyclone. The results obtained in this test series are given in Table 4.10 and a comparison of the SO_2 reductions obtained using the two different sizes of additive is shown in Fig. 4.12. Lower SO_2 reductions were obtained when using the finer limestone.

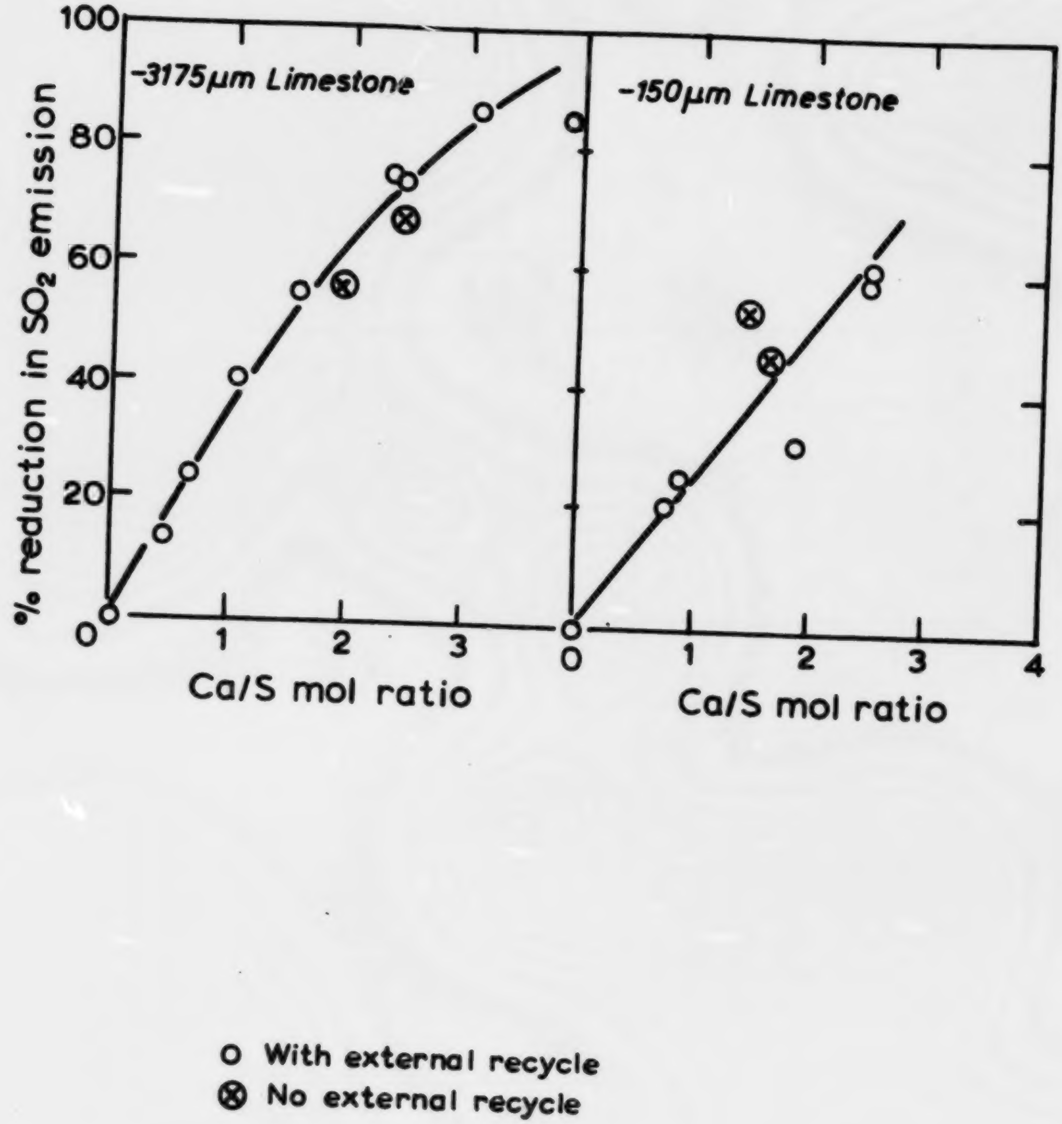


Fig. 4.12 Task III. SO_2 reduction in the 27in combustor for Limestone 18 and Pittsburgh coal. 8 ft/s. 1500-1575°F Test Series 2

Table 4.10. Summary of results obtained in Test Series 1 and 2 on 27 in combustor. (Task III)

Test No.	1	2.1	2.2	2.3	2.4	2.5	2.6	2.7	2.8	2.9.1	2.9.2	2.10	2.11	2.12	2.13	2.14	2.15	2.16.1	2.16.2
Operating conditions																			
Acceptor	Nil	L	L	L	L	L	L	L	L	L	L	Nil	L	L	L	L	L	L	L
Acceptor size	-	C	C	C	F	F	F	F	F	F	F	-	C	C	C	C	C	C	C
Ca/S mol ratio	0	1.58	0.44	3.09	1.86	0.88	2.47	0.74	2.47	1.63	1.45	0	1.09	2.37	3.89	0.62	2.45	1.93	2.47
Fluidising velocity, ft/s	8	8	8	8	8	8	8	8	8	8	8	8	8	8	8	8	8	8	8
External fines recycle	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	No	No	Yes	Yes	Yes	Yes	Yes	Yes	No	No
Bed temperature, ^{o}F	1510	1500	1510	1530	1560	1570	1550	1550	1570	1564	1550	1570	1560	1550	1560	1550	1560	1500	1520
Bed weight, lb	280	250	270	220	210	210	220	230	240	310	250	270	260	220	210	270	210	280	210
Gas composition																			
CO_2 % v/v	14.6	14.3	14.1	14.3	14.6	14.8	14.1	14.7	13.9	14.3	11.9	14.9	16.2	15.2	16.9	14.8	15.4	13.7	10.7
CO % v/v	0.72	0.66	0.68	0.69	0.66	0.65	0.72	0.69	0.71	0.54	0.57	0.70	0.68	0.71	0.67	0.75	0.71	0.64	0.48
O_2 % v/v	3.2	3.7	3.5	2.8	3.9	3.5	3.8	3.9	3.8	4.2	7.6	3.5	3.4	3.6	3.6	3.6	3.8	4.0	7.6
SO_2 ppm v/v	2050	930	1760	290	1370	1520	830	1610	790	1110	940	1680	1220	500	310	1550	530	910	680
NO_x ppm v/v	530	430	-	-	-	380	490	500	390	-	-	-	-	-	-	-	-	-	-
Unburnt carbon %	16	14	16	16	14	9	11	18	7*	20*	7+	6*	13	12	11	9*	11	16*	16*
Sulphur retention %	21	69	42	91	52	46	71	44	72	62	57	40	59	83	90	48	83	72	72
SO_2 reduction %	0	55	14	86	32	26	59	21	61	46	54	18	40	76	85	24	74	56	67

Acceptor: L denotes Limestone 18.

Acceptor size: C denotes -3175 micron, F denotes -150 micron.

* No estimate of unburnt carbon in exhaust dust is available.

+ No estimate of unburnt carbon in cyclone fines available.

Table 4.11. Summary of results obtained in Test Series 3 on the 27 in combustor. (Task III)

Test No.	3.1	3.2	3.3	3.4	3.5	3.6	3.7
Operating conditions							
Acceptor	L	L	L	L	L	L	D
Acceptor size	C	C	C	C	C	F	M
Ca/S mol ratio	2.68	2.69	2.80	2.63	2.67	2.66	1.74
Fluidising velocity ft/s	6	11	7	11	8	6	8
External fines recycle	Yes	Yes	No	No	Yes	Yes	Yes
Bed temperature, ^{o}F	1530	1570	1550	1550	1660	1560	1550
Bed weight, lb	220	210	220	260	200	260	250
Gas composition							
CO_2 % v/v	13.2	14.9	14.9	13.5	14.0	14.5	14.3
CO % v/v	0.69	0.65	0.63	0.57	0.64	0.72	0.63
O_2 % v/v	3.7	5.2	5.1	6.1	4.4	3.6	4.4
SO_2 ppm v/v	300	480	380	480	860	340	640
NO_x ppm v/v	-	330	510	410	500	470	530
Unburnt carbon %	10	8	12	15	6	14	15
Sulphur retention %	90	80	85	81	66	88	76
SO_2 reduction %	85	77	82	77	58	83	69

Acceptor: L denotes Limestone 18, D denotes Dolomite 1337.

Acceptor size: C denotes -3175 micron, M denotes -1587 micron,
F denotes -150 micron.

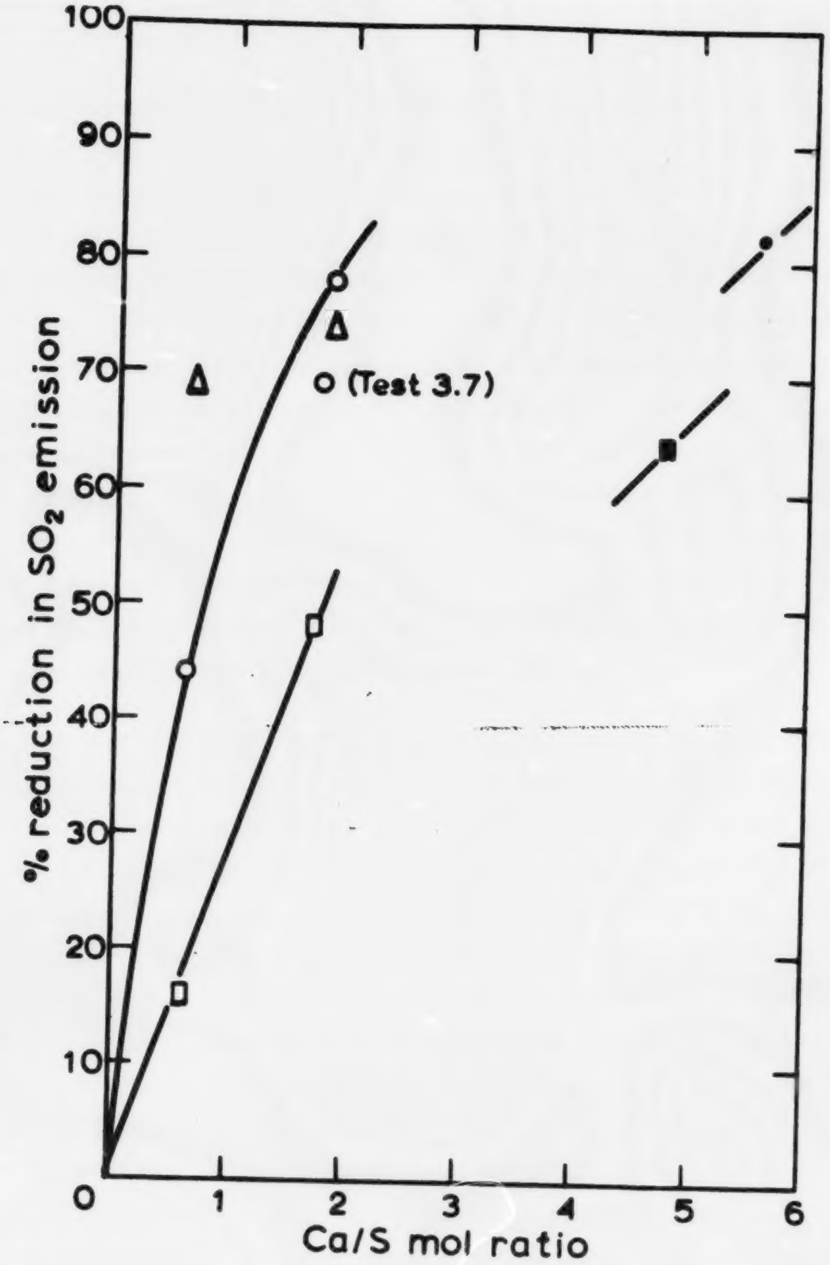
Table 4.12 Summary of results obtained in Test Series 4 on the 27 in combustor. (Task III)

Test No.	4.1	4.2	4.3	4.4	4.5	4.6	4.7	4.8	4.9
Operating conditions									
Acceptor	L	D	D	D	D	D	D	D	D
Acceptor size	C	M	M	M	M	M	M	M	M
Ca/S mol ratio	2.94	1.89	1.88	0.62	0.61	1.79	0.66	4.78	5.56
Fluidising velocity, ft/s	8	8	8	8	8	8	8	8	8
External fines recycle	Yes	Yes	Yes	Yes	Yes	Yes	Yes	No	No
Bed temperature, °F	1430	1420	1540	1560	1680	1680	1430	1650	1550
Bed weight, lb	350	310	210	230	200	180	250	200	210
Gas composition									
CO_2 % v/v	12.3	14.5	13.7	12.3	12.9	14.1	13.1	17.5	14.8
CO % v/v	0.64	0.60	0.72	0.74	0.75	0.69	0.63	0.75	0.64
O_2 % v/v	4.0	4.5	4.3	3.8	4.1	3.8	4.4	3.7	5.6
SO_2 ppm v/v	550	530	450	1160	1730	1060	650	750	370
NO_x ppm v/v	410	-	480	-	-	-	-	480	480
Unburnt carbon %	24*	8*	5*	0.4*	5*	5*	5*	7*	29*
Sulphur retention %	78	78	82	54	31	58	72	69	82
SO_2 reduction %	73	74	78	44	16	48	69	64	82

Acceptor: L denotes Limestone 18, D denotes Dolomite 1337.

Acceptor size: C denotes -3175 micron, M denotes -1587 micron.

* No estimate of unburnt carbon in exhaust dust is available.



Bed temperature: °F	1420	1550	1650	1680
With internal recycle	–	●	■	–
With internal and external recycle	Δ	○	–	□

Fig. 4.13 Task III. SO_2 reduction in the 27 in combustor for Dolomite 1337 and Pittsburgh coal 8 ft/s. (Test Series 4)

The main objective of Test Series 3 was to determine the effect of fluidising velocity using Limestone 18 by operating at 6½ and 11 ft/s, both with and without external fines recycle. Three additional tests were carried out with (a) a high bed temperature, (b) fine limestone and (c) Dolomite 1337. The results obtained in Test Series 3 are given in Table 4.11. With -3175 micron Limestone 18, the SO_2 emission increased slightly with increasing fluidising velocity, (Tests 3.1 to 3.4). Although recycle of fines from the external cyclone increased SO_2 reduction when operating at 6½ ft/s, it had no effect at the higher velocity of 11 ft/s. The SO_2 reduction obtained with fine stone at 6½ ft/s, (Test 3.6) was only slightly (2%) below that obtained with coarse stone This is in contrast to the large difference at 8 ft/s in Test Series 2. An attempt to operate at a fluidising velocity of 4 ft/s was abandoned after partial de-fluidisation occurred.

The main objective of Test Series 4 was to determine the effect of temperature on SO_2 reduction using Dolomite 1337 with and without external fines recycle. A single test was also carried out with Limestone 18 at a low bed temperature. The results are given in Table 4.12 and the SO_2 reductions obtained with Dolomite 1337 are plotted in Fig. 4.1[illegible]. The SO_2 reduction obtained in Test 4.7 is high, corresponding to about 100% utilisation of the stone, but there is no reason to suspect the validity of this test. The SO_2 reductions obtained at 1650-1680°F were considerably lower than those at both 1420 and 1550°F A comparison between the results at 1420 and 1550°F indicates that the effect of temperature is dependent on the Ca/S mol ratio, with optimum temperatures of about 1550°F at a ratio of 1.8 and of 1420°F at a ratio of 0.65. Fig. 4.13 shows that external fines recycle improved the SO_2 reduction at a fluidising velocity of 8 ft/s.

4.5 The 12 in corrosion combustor (Task IV)

The work carried out on the corrosion combustor is described in detail in Appendix IV.

4.5.1 Description of the plant

A flow diagram of the 12 in corrosion combustor plant is shown in Fig. 4.14 and the details of the combustor vessel are given in Fig. 4.15. The combustor was a 8 ft high mild steel column, refractory lined, with an internal cross section of 12 in square. The air distributor comprised a plate with 9 short vertical tubes arranged on a 4½ in square pitch, each tube having six ⅛ in diameter holes drilled horizontally, around the top Coal was injected at the centre of the combustor just above the air distributor nozzles. When limestone addition was required, the limestone was pre-mixed with the coal.

A constant bed height was maintained by a weir, the excess bed ash passing into a sealed hopper. The off-gases passed through an internal primary cyclone and external high efficiency secondary cyclone and then to the stack. Fines from the internal cyclone were recycled to the bed by means of a dip-leg.

Four rows of 2 in diameter air-cooled tubes were immersed in the bed on a 6 in triangular pitch; these removed the excess heat generated by combustion. Four of these tubes comprised corrosion specimen assemblies and these were cooled to the required test temperatures. Two specimen tubes were also situated in the freeboard 2 ft above the top of the ash bed. The construction of these specimen tube assemblies is described in section 4.1.3

The plant was designed to operate continuously for extended periods with a minimum of staff and was fully automated with comprehensive safety systems. Mass balances were normally carried out over a period of 100 h. Gas samples were taken from the freeboard, about 3 ft above the bed surface, for analysis of CO_2, O_2, CO and CH_4 by chromatograph. Other gas samples were taken after the secondary cyclone. These were analysed for SO_2 by the iodine and hydrogen peroxide methods, for SO_3 by the 'Shell Condensation' method and also for Na, K and Cl^-. All the outlet solids streams were sampled and solids samples could also be extracted directly from the bed.

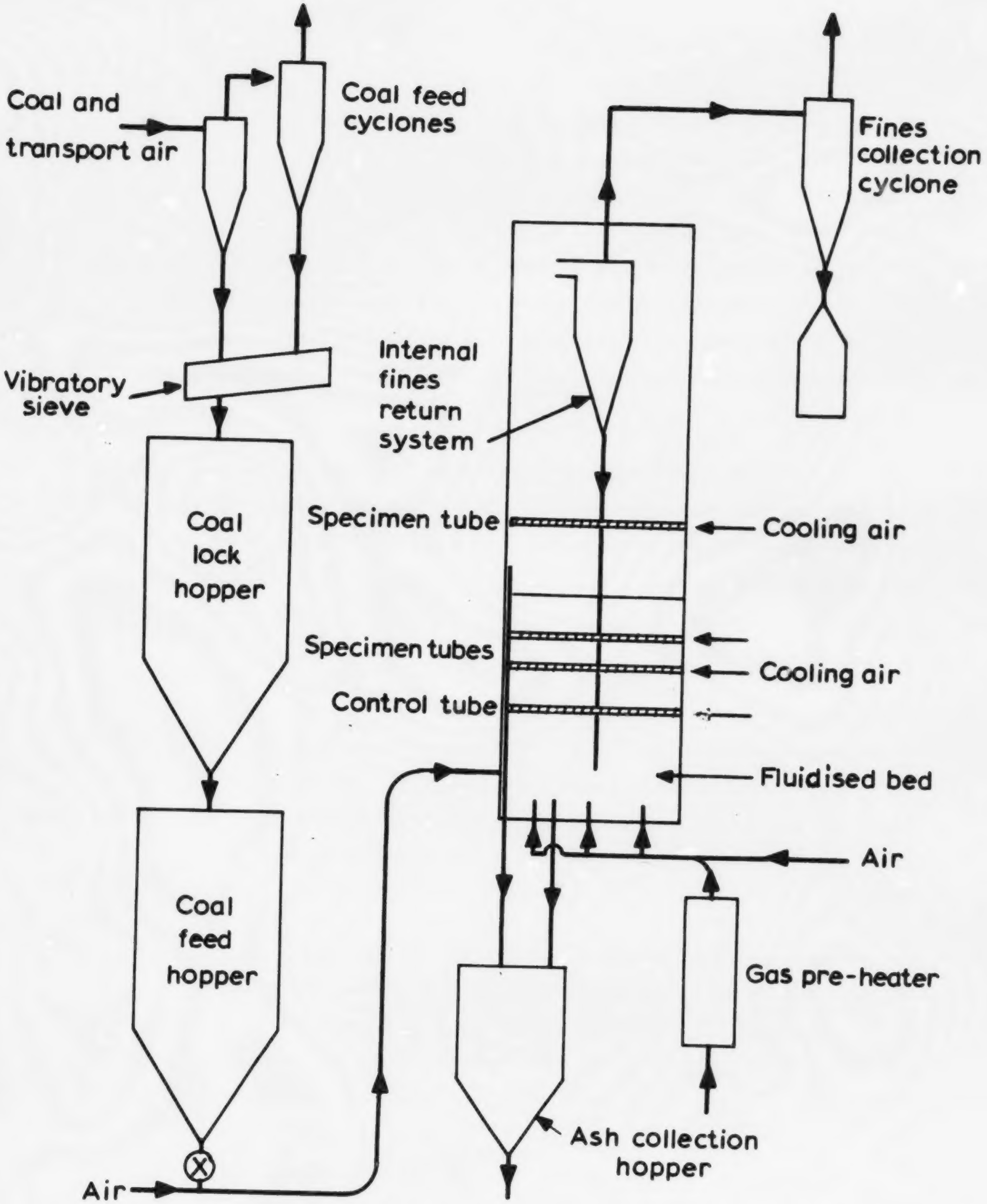

Coal and
transport air
Coal feed
cyclones
Fines
collection
cyclone
Internal
fines
return
system
Vibratory
sieve
Coal
lock
hopper
Specimen tube
Cooling air
Specimen tubes
Cooling air
Control tube
Fluidised bed
Air
Coal
feed
hopper
Gas pre-heater
Ash collection
hopper
Air

Fig. 4. 14 Task IV. Flow diagram of 12 in. corrosion combustor plant

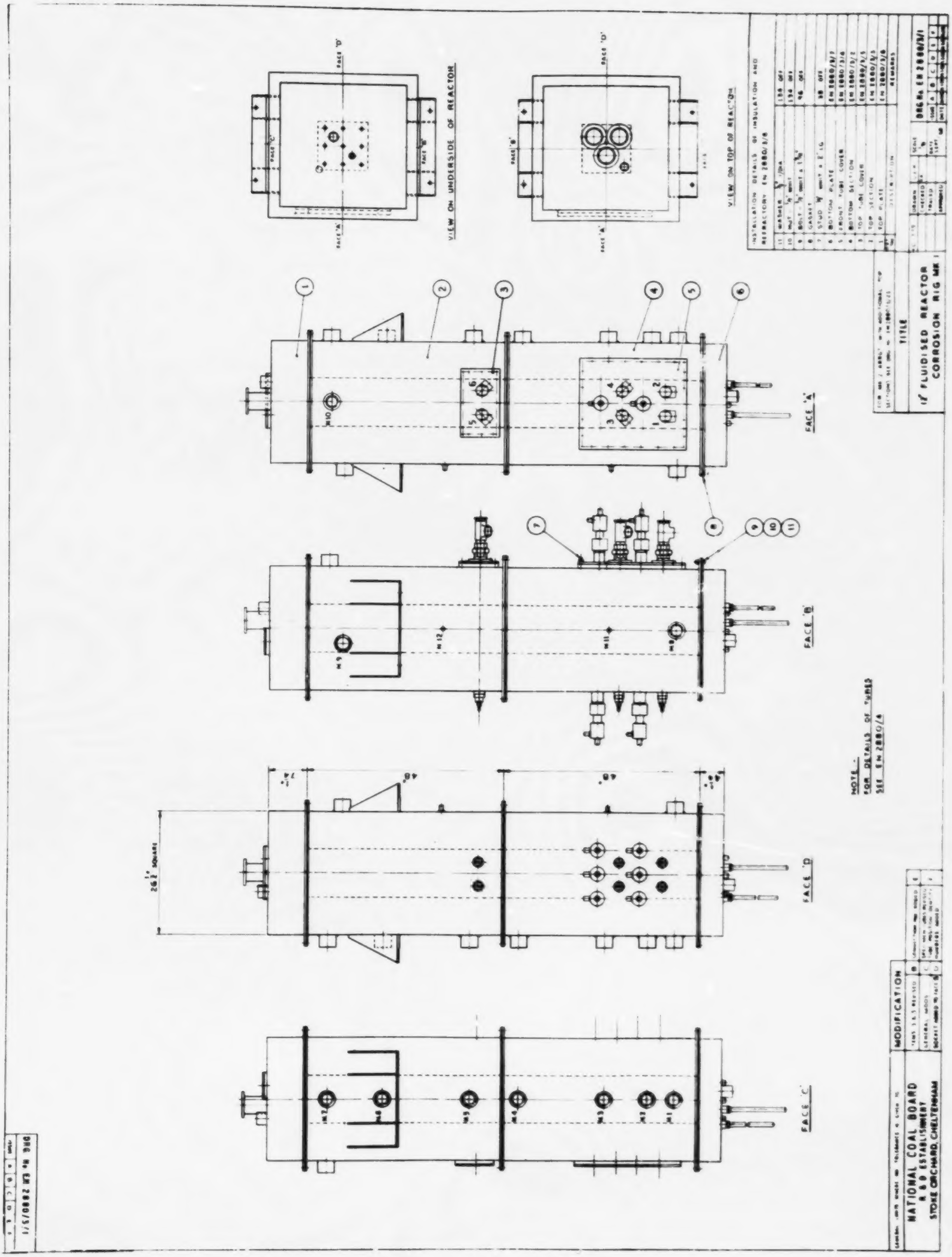

VIEW ON UNDERSIDE OF REACTOR
VIEW ON TOP OF REACTOR
FACE 'A'
FACE 'B'
FACE 'C'
FACE 'D'
FACE 'B'
1
2
3
4
5
6
7
8
9
10
11
26 1/2" SQUARE
NOTE - FOR DETAILS OF TUBES SEE EN 2880/4
INSTALLATION DETAILS OF INSULATION AND REFRACTORY EN 2880/3/8
WASHER
NUT
BOLT
GASKET
STUD
BOTTOM PLATE
FRONT TUBE COVER
BOTTOM SECTION
TOP TUBE COVER
TOP SECTION
TOP PLATE
DESCRIPTION
REMARKS
TITLE
12" FLUIDISED REACTOR CORROSION RIG MK I
DRG No EN 2880/3/1
MODIFICATION
NATIONAL COAL BOARD
R & D ESTABLISHMENT
STOKE ORCHARD, CHELTENHAM
DRG No EN 2880/3/1

Fig. 4.15 Task IV The 12in. corrosion combustor

4.5.2 Experimental programme

Three corrosion tests were carried out and these were designated Test Series 1, 2 and 3, as shown in Table 4.1. Each test series consisted of an extended period of operation under nominal constant standard conditions. These were a fluidising velocity of 3 ft/s, a bed temperature of 1560°F, a bed depth of 2 ft, total recycle of primary cyclone fines and an oxygen concentration in the flue gas of about 2%. Test Series 1 and 2 were carried out to obtain corrosion and deposition data using Pittsburgh coal without additive and were of 100 h and 500 h duration, respectively. Test Series 3 was carried out to determine the effect on corrosion, if any, of addition of Limestone 18 to the bed and was in all other respects a duplicate of Test Series 2. The coal and limestone were both prepared to a top size of 1680 μm.

4.5.3 Results

The data on corrosion are given in Section 4.7 together with corrosion data from other pilot plants.

4.5.3.1 Test Series 1 : 100 h test without limestone

The combustor was operated continuously except for one shut-down of 6 h duration caused by a coal feed stoppage due to the coal feed rotary valve jamming. A short preliminary test had shown that with Pittsburgh coal, coking would occur in an uncooled coal feed pipe. A new water-cooled feed pipe was used in Test Series 1 and this overcame the problem of coking. However it was apparent that the new position of the pipe led to bed ash being occasionally transported up the cyclone dip-leg. Thus it was necessary to add -1680 μm shale daily in order to maintain the required bed height The results, other than corrosion data, are summarised in Table 4.13.

4.5.3.2 Test Series 2 : 500 h test without limestone

The combustor operated continuously except for one short interruption of a few seconds, which was the result of a power cut. The position of the water cooled probe had been changed, with the result that there was an overflow of bed ash during the test. However the combustion efficiency was only slightly better than in Test Series 1, indicating that the fines recycle system may not

Table 4.13 Summary of results obtained on 12 in corrosion combustor (Task IV)

Coal	Pittsburgh
Additive	Limestone 18
Fluidising velocity	3 ft/s
Bed temperature	1560°F
Bed depth	2 ft
Top size of coal and additive	1680 μm

Test Series	1	2		3	
Duration of test, h	100	500		465	
Mass balance period, h	0-100	0-115	283-383	0-100	334-434
Oxygen in off-gas, %	1.9	2.3	2.1	2.1	2.4
Unburnt carbon loss, %	8.2	6.5	7.0	6.3	1.2
Off-gas temp, °F	1425	1475	1475	1410	1410
Ca/S mol ratio	0	0	0	2.4	1.9
SO_2 in off-gas, ppm v/v	2270	2090	2050	200	52
SO_2 reduction, %	0	0	0	90.5	97.5
CO in off-gas, ppm v/v	330	660	900	600	600
Cl^- in off-gas, ppm v/v	57	64	74	55	-
Na in off-gas, ppm wt	6.4	2.7	4.7	4.5	3.7
K in off-gas, ppm wt.	3.0	1.2	1.6	0.7	0.9
Ca in off-gas, ppm wt	69	16	21	98	135
SO_3 in off-gas, ppm v/v	5	5	5	1	7

have been functioning correctly. Two mass balances were carried out during the test and the results are summarised in Table 4.13. The performance of the plant remained constant during the 500 h test.

4.5.3.3 Test Series 3 : 500 h test with limestone addition

The combustor operated continuously, except for four minor interruptions of several minutes duration during which the bed temperature did not fall below 1400°F, until 35 h before the planned end of the test. A failure of the coal feed electronic control unit then caused the plant to be shut down. For three hours before shut-down the combustion conditions varied between reducing and oxidising as attempts were made to rectify the fault. Two mass balances of 100 h were carried out during the test and the results are summarised in Table 4.13. These results suggest that, sometime between the two balance periods, the fines recycle system began to function correctly. Thus the unburnt carbon loss fell to 1.2% and the SO_2 reduction increased to 97.5%. despite a lower Ca/S mol ratio.

4.6 The 6 in combustor (Task V)

The work carried out on the 6 in combustor is described in detail in Appendix V.

4.6.1 Description of the plant

A flow diagram of the 6 in combustor plant is shown in Fig. 4.16 and details of the bed section of the combustor are shown in Fig. 4.17. The combustor was of circular cross-section and was constructed throughout of stainless steel. The lower section was 6 in. in diameter and 6 ft high; this expanded over approximately 1 ft into a 1 ft 5 in diameter section, 4 ft in height. The whole combustor could be heated electrically by external wall heaters. These were used for start-up and then to maintain a uniform temperature throughout the freeboard. Air supplied from a plenum chamber, passed through a distributor plate made from a drilled flat plate covered with three layers of ¾ in diameter alumina balls. The pre-mixed coal/additive feed was pneumatically conveyed to the bed, which it entered tangentially, approximately ¾ in above the alumina balls. Excess heat was removed by a water-cooled metal coil immersed in the fluidised bed. The bed height was maintained constant by emptying surplus ash through a tube in the centre of the distributor.

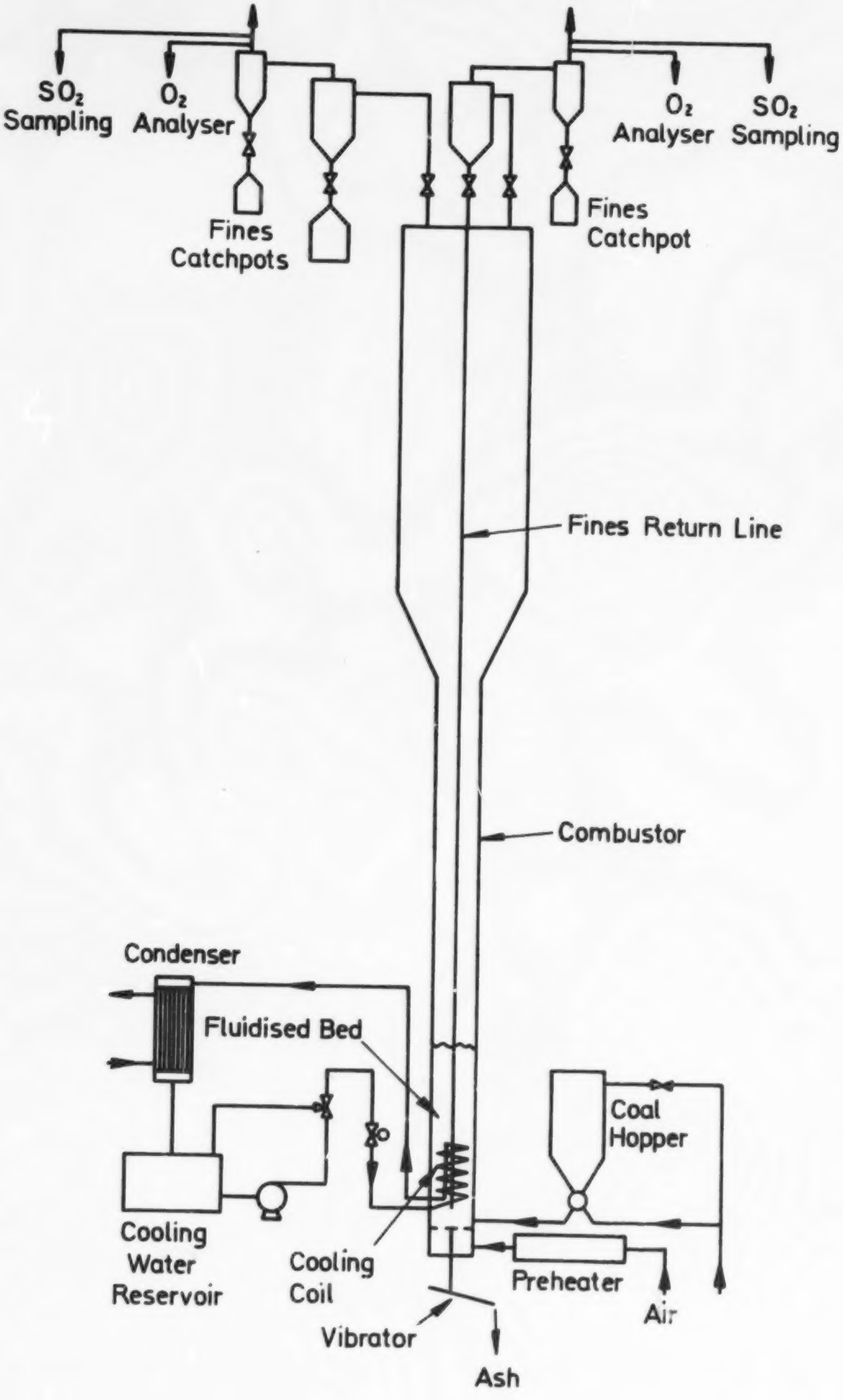

SO2 Sampling
O2 Analyser
Fines Catchpots
O2 Analyser
SO2 Sampling
Fines Catchpot
Fines Return Line
Combustor
Condenser
Fluidised Bed
Coal Hopper
Cooling Water Reservoir
Cooling Coil
Preheater
Air
Vibrator
Ash

Fig. 4. 16 Task V. Flow diagram of 6in. combustor plant

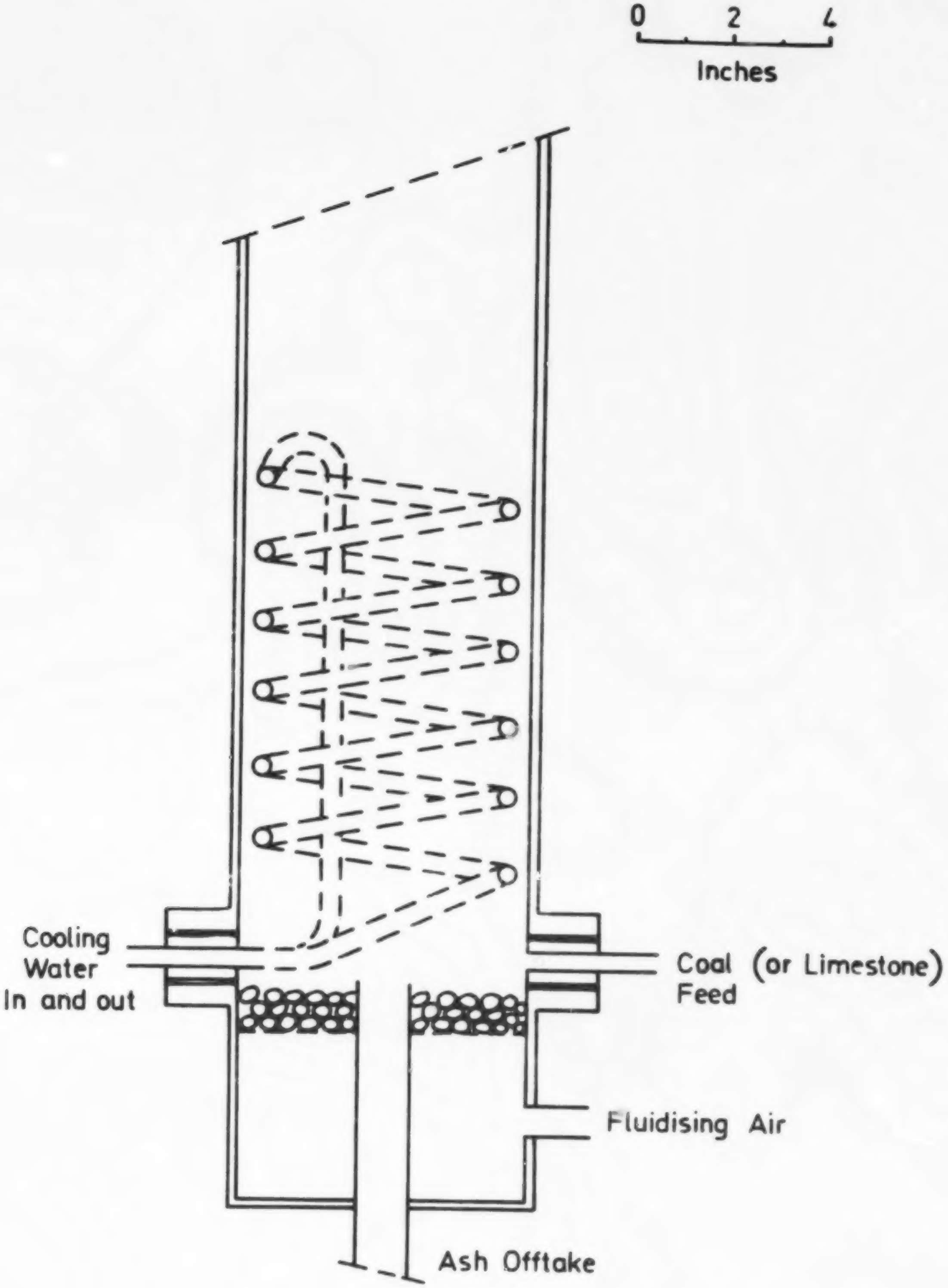

0 2 4
Inches
Cooling Water In and out
Coal (or Limestone) Feed
Fluidising Air
Ash Offtake

Fig. 4. 17 Task V. Detail of bed section of 6in. combustor

The gases leaving the combustor could be directed through two alternative cyclone systems, both comprising primary and secondary cyclones, for operation with or without fines recycle. In the 'with recycle' system the primary cyclone was vertically above the bed and the fines were recycled via a dip-leg. Gas samples were withdrawn at a point about 2 ft after each secondary cyclone, as appropriate, and bubbled through iodine or H_2O_2 solution for determination of SO_2. Samples were also taken for analysis of O_2, CO, CO_2 and CH_4 by chromatograph.

Each test was carried out as a one day (16 hour) run comprising plant start-up, approach to equilibrium, a six hour mass balance and shut down.

4.6.2 Experimental programme

Tests were carried out using all of the four coals, Illinois, Pittsburgh, Park Hill and Welbeck, and the three limestones. A total of forty one-day tests was carried out and these were grouped into five test series as shown in Table 4.1. Except for two tests with fine Limestone 1359, all the coals and limestones were prepared to minus 10 BS mesh (1680 µm). Typical size distributions of the materials as prepared are given in Table 4.14.

Table 4.14 Typical size distributions of prepared coals and limestones (Task V)

Material	Percentage in size range (sizes in µm)						Median µm
	+1680	+500 -1680	+250 -500	+125 -250	+63 -125	-63	
Illinois coal	0.3	49.2	25.1	13.9	6.1	5.4	494
Pittsburgh coal	0	36.6	23.5	17.0	12.8	10.1	340
Welbeck coal	0	29.4	37.1	17.3	6.4	9.8	364
Park Hill coal	0	63.5	16.7	8.9	4.9	6.0	716
Limestone 18	0.1	21.0	22.0	22.5	12.2	22.2	207
Limestone 1359	0.1	36.7	24.8	16.6	8.7	13.1	353
U.K. Limestone	0.5	52.1	19.1	10.1	7.2	11.0	537

4.6.3 Results

4.6.3.1 U.K. limestone with Welbeck, Park Hill, Illinois and Pittsburgh coals

The effect of the Ca/S mol ratio on SO_2 reduction was determined for all four coals with U.K. limestone at a fluidising velocity of 3 ft/s and at 1470°F. The results obtained are summarised in Table 4.15 and are plotted in Fig. 4.18. Possible reasons for the higher SO_2 reduction with Welbeck coal than with the other three coals are discussed in section 7.1.11. Additional tests with Welbeck coal, included in Table 4.15, showed an improvement in SO_2 reduction when the fluidising velocity was lowered to 2 ft/s, but no effect of internal fines recycle or of substoichiometric combustion conditions.

4.6.3.2 Limestone 1359 with Illinois coal

The effect of the Ca/S mol ratio on SO_2 reduction was determined for Limestone 1359 with Illinois coal in order to allow comparison (i) between Limestone 18 and Limestone 1359 and (ii) between the CRE and ANL 6 in combustors. The operating conditions and results obtained are summarised in Table 4.16, and the SO_2 reductions at 1470°F are plotted in Fig. 4.19. The SO_2 reduction was improved by deepening the bed from 2 to 3 ft and by the use of finely crushed (-125 μm) limestone. The SO_2 reductions obtained at 1290°F were very low (15% and 18% at Ca/S mol ratios of 1.1 and 2.2 respectively) and clearly showed that operation at this temperature is unsatisfactory with Limestone 1359. Limestone 1359 was less effective than U.K. limestone (Fig. 7.16).

4.6.3.3 Limestone 18 with Pittsburgh and Welbeck coals

Limestone 18 was used in five tests with Pittsburgh coal and in a single test with Welbeck coal. The operating conditions and results are summarised in Table 4.17. With Pittsburgh coal the Limestone 18 was more effective than U.K. limestone (Fig. 7.1[illegible]). The single result with Welbeck suggests that this might not be the case with Welbeck coal, but a meaningful comparison is not possible.

Comparative tests at a Ca/S mol ratio of 0.8 starting with (a) lime-free ash, (b) lime-free shale, (c) lime rich ash from a test at Ca/S of 2.6, confirmed that equilibrium conditions were being reached in the short time allowed for stabilisation.

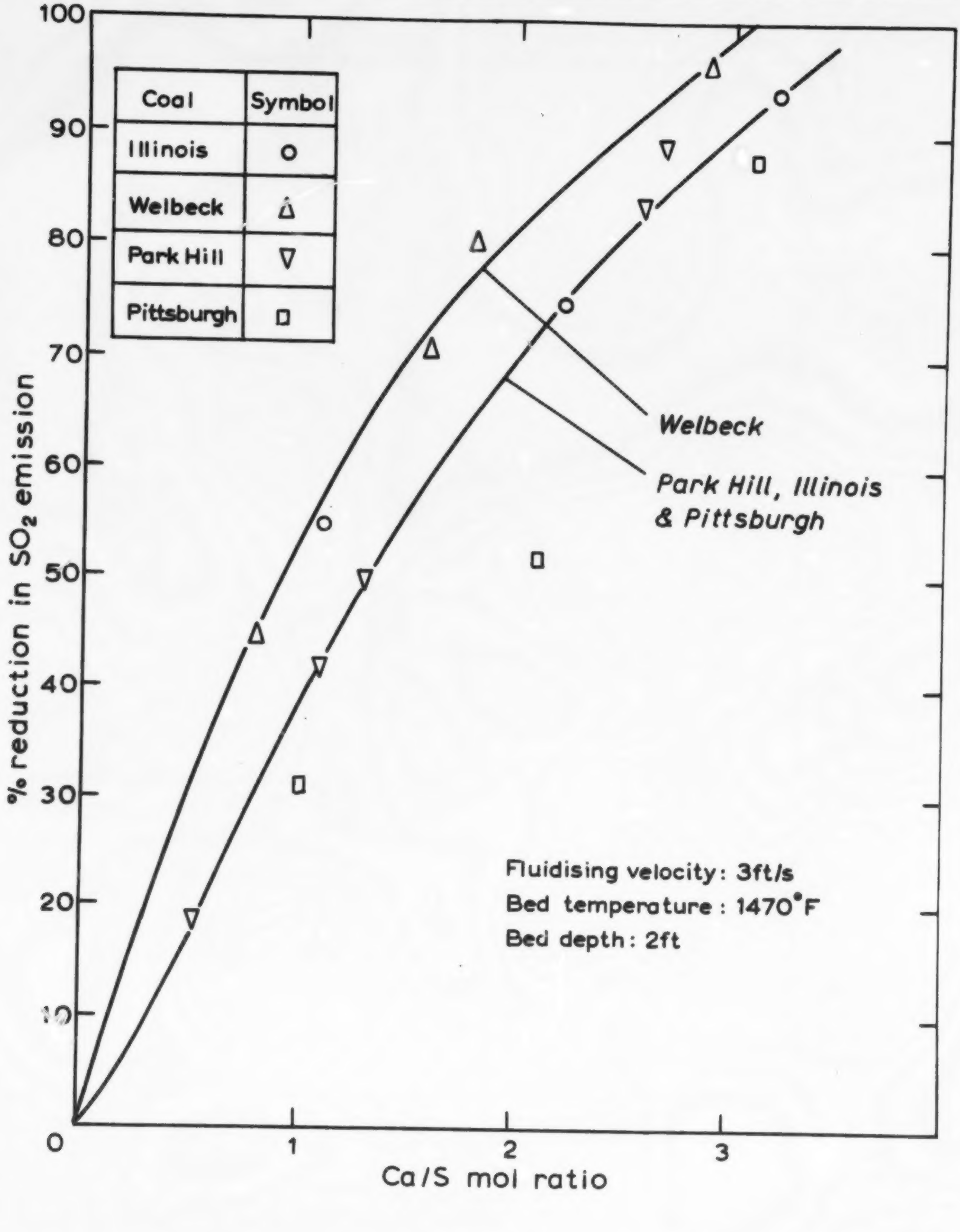


Fig. 4.18 Task V. SO_2 reduction in the 6in. combustor for U.K. limestone with different coals

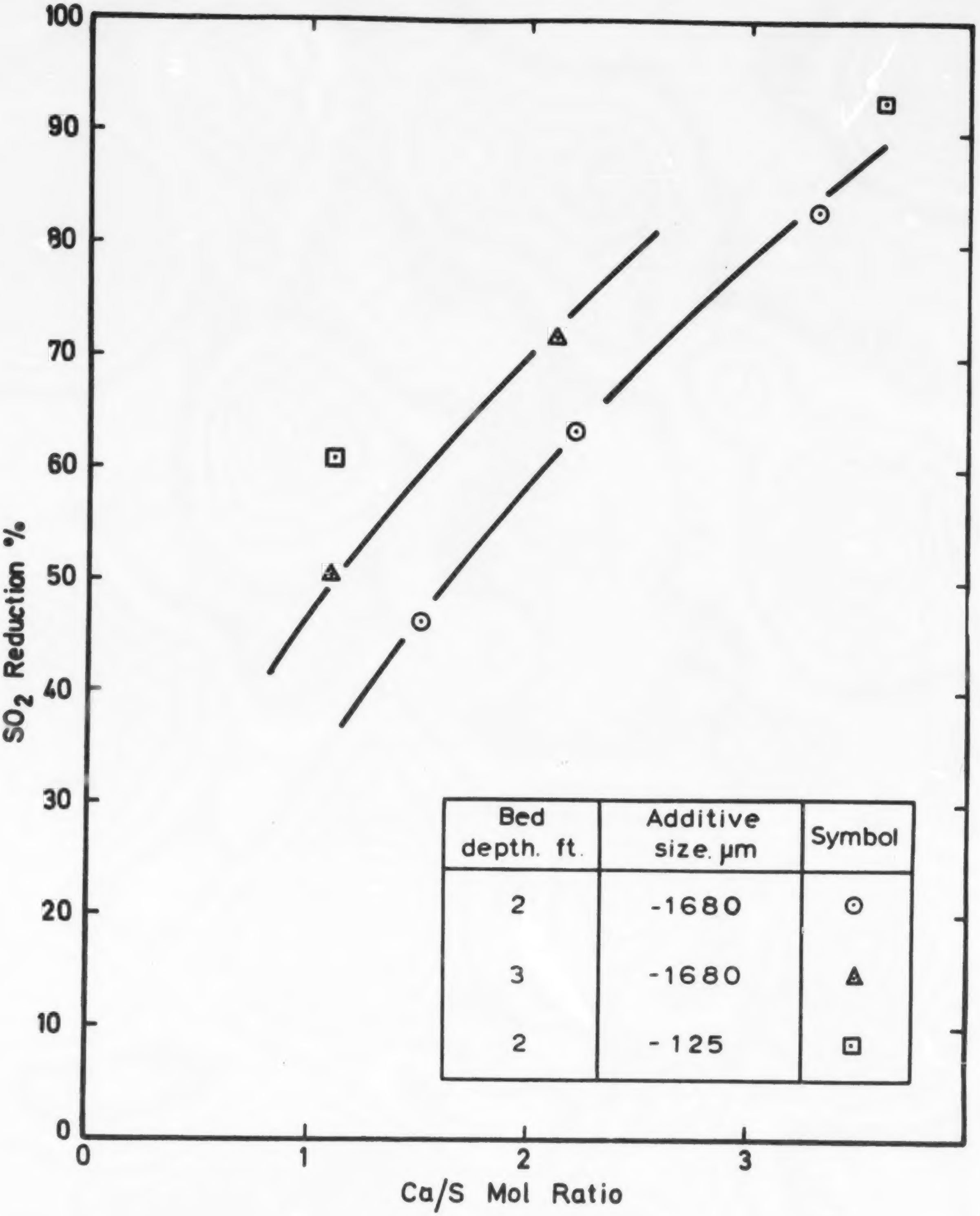


Fig. 4.19 Task V. SO_2 reduction in the 6in. combustor for limestone 1359 and Illinois coal 3 ft/s 1470 °F

Table 4.15. Summary of results obtained on the 6 in. combustor with U.K. limestone and Welbeck, Park Hill, Illinois and Pittsburgh coals at a bed temperature of 1470°F and a bed height of 2 ft. (Task V)

Test No.	1.5	1.6	1.7	1.8	2.1*	2.2*	2.3	2.4	2.5	2.6	2.7†	2.8	2.9	2.10	2.11	2.12	2.13	2.14	2.15*	4.1	4.2	4.3	4.4	5.1
Coal type	Illinois				Welbeck								Park Hill							Pittsburgh				Welbeck
Fluidising velocity, ft/s	3	3	3	3	2	2	2	3	3	3	3	2	3	3	3	3	3	3	3	3	3	3	3	3
Oxygen in off gas, %	2.6	2.2	2.3	2.6	3.1	3.1	3.1	3.1	2.3	2.2	0.3	2.6	2.0	2.5	2.0	2.3	2.1	2.5	2.0	2.3	2.4	2.2	2.4	2.8
Unburnt carbon loss, %	4.6	3.4	3.7	4.5	2.6	2.6	6.9	7.9	7.1	5.3	13.4	5.1	10.9	9.4	10.4	10.1	10.3	9.2	8.7	6.3	9.5	10.7	8.7	14.0
Ca/S mol ratio	1.1	2.2	3.2	0	0	0.8	0.8	0.8	1.8	2.9	0.8	1.8	0.5	1.3	2.7	0	1.1	2.6	0.8	0	1.0	2.1	3.1	1.6
SO_2, ppm	1785	1000	229	3896	1087	488	513	599	207	33	612	158	1690	1045	237	2091	1210	322	547	1980	1372	938	241	342
S retention, %	55	66	94	1	7	58	56	54	82	98	61	86	15	30	79	12	49	86	54	5	41	57	90	79
SO_2 reduction, %	55	67	94	0	0	55	52	45	81	97	48	85	-	25	78	0	42	84	50	0	31	52	88	71
Cl^-, ppm	179	182	152	160	438	408	456	267	411	289	325	410	136	89	68	175	149	132	337	121	75	89	95	303
NH_3, ppm	34	25	17	26	11	10	6	-	51	-	-	16	15	25	60	31	36	30	7	-	-	-	-	12

* Tests with primary fines recycle

† Test at substoichiometric conditions

Table 4.16 Summary of results obtained on the 6 in combustor with Limestone 1359 Illinois coal (Task V)

Test No.	1.1	1.2	1.3	1.4	3.1	3.2	3.3	3.4	3.5*	3.6*
Fluidising velocity	3	3	3	3	3	3	3	3	3	3
Bed temperature, ^{o}F	1470	1470	1470	1470	1290	1290	1470	1470	1470	1470
Bed height, ft	2	2	2	2	2	2	3	3	2	2
Oxygen in off gas, %	2.9	2.8	2.6	2.9	2.7	2.4	2.7	2.6	2.4	2.5
Unburnt carbon loss, %	4.2	3.8	3.3	3.3	7.3	6.5	5.0	4.9	4.1	3.6
Ca/S mol ratio	0	1.5	2.2	3.3	1.1	2.2	1.1	2.1	1.1	3.6
SO_2, ppm	4023	2118	1450	680	3376	3245	1930	1136	1523	278
S retention, %	0	47	64	78	24	26	49	70	61	92
SO_2 reduction, %	0	47	63	78	15	18	51	72	61	93
Cl^-, ppm	134	126	150	145	141	161	126	125	139	97
NH_3, ppm	20	90	9	23	34	23	12	11	21	9

* Tests with -125 μm limestone.

Table 4.17 Summary of results obtained on the 6 in combustor with Limestone 18 and Pittsburgh and Welbeck coals at a temperature of 1470°F and a bed depth of 2 ft (Task V)

Test No.	4.1	4.5	4.6	4.7	4.8*	4.9†	5.2
Coal Type	← Pittsburgh →						Welbeck
Fluidising velocity, ft/s	3	3	3	3	3	3	3
Oxygen in off gas, %	2.3	2.5	2.2	2.3	2.1	2.5	2.6
Unburnt carbon loss, %	6.3	8.6	9.2	7.6	9.4	11.1	11.9
Ca/S mol ratio	0	0.9	1.7	2.6	0.9	0.9	1.9
SO_2, ppm	1980	1137	581	185	1238	1115	236
S retention, %	5	50	75	92	55	60	85
SO_2 reduction, %	0	43	71	91	38	43	80
Cl^-, ppm	121	83	69	65	69	50	363
NH_3, ppm	-	0	-	21	22	24	3

* Test with lime rich bed.

† Test with shale bed.

Table 4.18. Typical Analyses of Alloys Tested

Material			Nominal Composition %												Normal* Operating Temp °F
Type	BSS	AISI No	Cr	Ni	C Max	Mn	P Max	S Max	Si Max	Mo	Ti	Al	Fe	Other	
Medium Carbon Steel	3059/5				0.25		0.05	0.05					Bal.		900
1% Cr, ½% Mo Steel	3059/ 620		1.00		0.15	0.7 max	0.05	0.05	0.6	0.50			Bal.		1050
2¼% Cr, 1% Mo Steel	3059/ 622		2.25		0.15	0.7 max.	0.04	0.04	0.5	1.00			Bal.		1100
12% Cr Steel	EN 56A	410	12		0.15	1.0 max.	0.04	0.03	1.0				Bal.		-
Austenitic 316	EN 58J	316	17	12	0.09	2.0 max.	0.05	0.05	0.2	2.5			Bal.		-
Austenitic 347	EN 58G	347	18	11	0.08	2.0 max.	0.05	0.03	1.0				Bal.	Nb 10 XC min	1220
Esshete 1250			15	10	0.15	6.0	0.04	0.03	1.0	1.0			Bal.	Nb 1%	-
Nimonic PE 16			17	43	0.10			0.02	0.3	3.0	1.2	1.2	Bal.		-

*Ref. CEGB, Modern Power Station Practice, Vol 2

4.7 Results of Corrosion Investigations

The corrosion of metal specimens at various temperatures was investigated under Task II (48 in x 24 in pressurised combustor), Task III (27 in combustor) and Task IV (12 in combustor), the latter combustor being designed specifically for corrosion work. Table 4.18 gives analyses of the metals investigated.

4.7.1 Appearance of Steels after Tests

When the tubes and coupons were removed from the combustors they were examined visually. In general the condition of the fire-side surfaces appeared similar for all the tests.

Direct metallic erosion of specimen tubes by the ash particles had not occurred. This observation was expected because the particle velocities, associated with fluidising velocities of 2 ft/s to 8 ft/s, would be quite low. It has been shown that in conventional coal-fired boilers, flue gas velocities of around 100 ft/s are necessary before steel is eroded by particle impaction[3].

Visual examination of the test specimens also suggested that the scouring action by the ash particles was not sufficiently erosive to remove the protective oxide cover and expose clean metal surface to the environment. This was confirmed by the specimen weight loss results. These showed that the rate of corrosion decreased with time, thus indicating the formation of a stable protective oxide layer.

On the other hand, the presence of the fluidised bed did have some influence on the formation of deposits on the tubes. The tubes situated in the bed were mostly covered with a thin, even, hard and adherent deposit (<0.1 mm thick). A thicker (up to 1.5 mm) but more loosely adherent ash-type deposit was sometimes formed on the underside of the tubes cooled to 750-900°F which were situated close to a coal feed nozzle.

The underside of the tubes situated above the bed in the 12 in combustor (Task IV) were covered with a layer of fine ash, and coarse ash particles formed a layer on the top of these tubes. Both types of layer were loosely adherent and were not found on the tubes situated in the bed.

Table 4.19. Task II - Average weight loss of specimens

Test	Wt. loss in μg/cm^{2}h							
	Temp. ^{o}F	1% Cr	2½% Cr	12% Cr	Type 347	Type 316	Esshete 1250	PE 16
Series 1 (Welbeck + U.K. Dolomite) 100 h duration	660	24	35	2	4	1	-	-
	1020	-	-	2	4	4	4	4
	1160	357	307	5	4	5	7	3
	1350	-	-	5	8	8	30	5
	1460	-	-	-	17	16	50	8
Series 2 (Pittsburgh + Dolomite 1337) 81 h duration	630	99	151	18	7	8	-	8
	1140	-	-	16	28	23	48	14
	1330	-	-	18	48	54	210	36
	1460	-	-	-	109	124	215	43
Series 3 and 4 (Pittsburgh + Dolomite 1337) 145 h duration	750	24	31	4	6	3	-	3
	1030	-	-	8	6	15	7	6
	1220	-	-	11	12	40	60	11
	1450	-	-	-	18	14	90	40
Series 5 (Pittsburgh + Limestone 18 + Dolomite 1337) 100 h duration	700	50	31	-	-	-	-	-
	1040	-	-	4	20	8	14	6
	1200	-	-	4	13	4	76	14
	1450	-	-	-	45	20	60	45

Note: Towards the end of Test Series 2 the bed partially defluidised and some sintering of the bed occurred. This probably caused the higher weight losses for this test.

Table 4.20. Task III. Average weight loss of specimens

Test	Wt. loss in $\mu g/cm^2h$						
	Temp. °F	M.C.S.	2¼% Cr	12% Cr	Type 347	Type 316	Esshete 1250
Series 1B (Pittsburgh) 500 h duration	750	60	75	4	5	3	4
	930	400	-	7	6	4	8
	1110	-	-	3	-	3	7
	1290	-	-	4	9	10	16
Series 2 (Pittsburgh + Limestone 18) 1000 h duration	750	8	4	1	<1	<1	1
	930	36	38	3	1	1	1
	1110	-	270	2	2	3	4
	1290	-	-	3	5	9	12
Series 3 (Pittsburgh + Limestone 18) 500 h duration	750	10	14	2	<1	1	1
	930	-	30	2	<1	1	1

Note: Test Series 1A was terminated by a failure of the cooling medium after 147 hours. This resulted in the specimen tubes being grossly overheated for a short period and the weight losses were not representative. They have been omitted from the above Table.

Table 4.21. Task IV. Average weight losses of specimens

Test	Position	Wt. loss in $\mu g/cm^2h$							
		Temp °F	M.C.S.	2¼% Cr	12% Cr	Type 347	Type 316	Esshete 1250	PE 16
Series 1 (Pittsburgh) 100 h duration	In bed	690	91	92	–	–	1	2	–
		940	163	179	–	–	2	3	–
		1100	–	579	–	7	8	9	–
		1320	–	–	–	11	11	21	–
		1560	–	–	–	12	9	20	–
	In freeboard	780	62	74	–	–	1	2	–
		1340	–	–	–	5	4	10	–
		1500	–	–	–	3	2	4	–
Series 2 (Pittsburgh) 500 h duration	In bed	770	48	32	2	–	1	1	–
		920	88	78	6	–	2	1	–
		1090	–	539	5	3	3	4	–
		1310	–	–	3	3	4	6	3
		1560	–	–	308	7	5	7	3
	In freeboard	760	25	25	1	–	<1	<1	–
		1310	–	–	1	1	1	5	1
		1520	–	–	3	–	1	3	2
Series 3 (Pittsburgh + Limestone 18) 465 h duration	In bed	730	41	42	2	–	1	1	–
		930	84	98	6	–	2	2	–
		1100	–	222	3	2	2	3	–
		1320	–	–	7	6	6	13	5
		1560	–	–	475	3	2	3	2
	In freeboard	760	18	18	2	–	<1	<1	–
		1310	–	–	2	2	2	6	2
		1490	–	–	2	2	3	12	2

The layers of material on the tubes were no thicker after 500 or 1000 hour operation than they were after 100 hours. They were insignificant compared with those occurring in conventional powdered coal-fired boilers, and were predominantly ash.

There appeared to have been very little surface attack of the alloys tested at their usual operating temperatures. This includes the low alloys, namely, medium carbon and 2¼% Cr steels, which were only slightly blistered. These two alloys had somewhat thicker scales when tested above their normal maximum operating temperatures[4] of 800°F and 1000°F respectively.

4.7.2 Weight Loss Results

The weight loss results for all three Tasks are summarised in Tables 4.19, 4.20 and 4.21.

The maximum penetration rate on the fire side of conventional boiler tubing that can be tolerated is generally assumed to be about 1.5×10^{-6} in/h. This is equivalent to a specimen weight loss rate of 30 μg/cm^2 if there is no preferential loss around the circumference of the tube nor any intergranular penetration of the metal surface. This figure has been used as a guide in assessing data from the present experiments.

4.7.3 Metallographic Examination

Specimen rings and coupons were sectioned, mounted and polished. They were examined under a microscope and a few were also examined by electron probe microanalysis. For normal operating conditions, materials maintained at or below their accepted maximum working temperature in conventional plant did not suffer significant intergranular penetration by sulphur.

The surfaces of the austenitic steels from the 100 h tests were mostly smooth* with the exception of the coupons in Task IV held at 850°C in the bed. The low chromium steels exhibited somewhat rougher surfaces as might be expected from the higher specimen weight losses. The surfaces of the specimens from the 500 h and 1000 h tests were on the whole slightly rougher. There appeared to be little difference in the number or magnitude of surface irregularities between the tests.

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* defined as surface irregularities $\not>$ 4 μm.

The oxide layer for all steels was up to 10 μm thick with no significant effect of test duration or metal temperature

The austenitic steels showed little evidence of sulphide penetration at temperatures below 1110°F (maximum observed was 10 μm in isolated instances) and for test durations of up to 1000 h. In the range 1290°F to 1560°F sulphide penetration of 10 to 20 μm was general in 100 h tests and, exceptionally, up to 70 μm in the 1000 h test.

For the low chrome steels, penetration was generally absent in 100 h tests at temperatures below 930°F It was about 50 μm in 500 h tests at temperatures of 1110°F.

Specimens of 2¼% Cr held at 1110°F for 500 h in Test 2 of Task IV were examined by electron probe microanalysis, confirming sulphide penetration of about 50 μm

5. THE MATHEMATICAL MODEL (Task VI)

The mathematical model, and comparisons with the results of a number of test series and with results from work carried out by Pope, Evans and Robbins[5] are described in detail in Appendix 6.

The construction of a mathematical model to represent the sulphur retention process was embarked upon with the twin objectives of gaining an understanding of the behaviour of the plants in the experimental programme, and of developing a technique for use in extrapolating the results to other plants, fuels or limestones, for purposes of economic assessments.

It is assumed that the rate controlling process is transport within the additive particles rather than transport of SO_2 to the particle surface. The rate of mass of SO_2 absorbed per unit time per unit mass of additive has been related to the SO_2 concentration by means of a rate constant. Values of the rate constant have been determined in laboratory tests (Section 6.2.9) and related to particle size and degree of sulphation (Fig. 6.2) In the mathematical model these relationships have been assumed to apply to particles within the fluidised bed combustor.

In general form, the model falls into two broad sections. The first section calculates from the input data the terminal velocities of particles in up to ten size groups, and thence the bed composition in terms of weights of ash and limestone of different particle sizes. The mean residence time of each group of particles is also calculated. The second section evaluates the absorption of sulphur dioxide in and above the bed by an iterative procedure An initial value is assumed for the mean reactivity of the bed and from it are calculated the sulphur retention and the mean SO_2 concentration in the bed. Knowing the residence time of each close size fraction and the relationship between reactivity and degree of sulphation, the value of the degree of sulphation is calculated for each size fraction, such that the calculated total sulphur retention would be obtained with the calculated mean SO_2 concentration. An improved estimate of the mean bed reactivity is calculated from these values of degree of sulphation, and hence improved values of sulphur retention and mean SO_2 concentration are obtained. The procedure is repeated until a satisfactory degree of convergence is obtained, the whole process taking less than a minute of computer time.

The mathematical model predicts that the extent of sulphation of particles small enough to be elutriated from the bed should be very small compared with those particles which stay in the bed. However, the utilisation of the fine particles should be increased significantly by efficient recycling to the bed.

The utilisation of particles only just small enough to be elutriated from the bed is very sensitive to the value of the elutriation rate constant, which determines the residence time of these particles in the bed.

Whereas the comparisons with experimental tests using dolomite are on the whole good, it was obvious even before running the mathematical model that there would be difficulty in getting agreement in the case of the limestone tests. Considering, for example, the tests in Task V using Limestone 1359, for which the laboratory reaction rate measurements showed that the reactivity drops to zero at utilisations ranging from about 10% for the coarse particles to about 50% for the very fine particles. A mean value would be about 20%. In a typical test on the six inch diameter combustor, addition of this limestone at a Ca/S mol ratio of 1 gave a retention of about 45%: this was in spite of the fact that some 50% of the stone was of small enough size to be elutriated from the bed. Even if no limestone were elutriated, the retention could not be explained on the basis of the kinetic data.

It was obvious therefore that an attempt would have to be made to allow for the exposure of fresh, unsulphated stone by abrasion of the sulphated surface layer whose impermeability results in the limit to the utilisation capacity of the stone. A crude computational procedure for doing this has been introduced into the model by assuming that the sulphated particles consist of completely unsulphated cores surrounded by concentric shells of completely sulphated material. The rate at which particles are "regenerated" by attrition is calculated as the weight of particles in the bed divided by the time needed to reduce the particle diameter by an amount equal to double the shell thickness, and then multiplied by the chances that a particle will stay in the bed for a sufficiently long period of time for this to occur.

The mean utilisation used in the absorption calculation for deriving the reaction rate is then reduced by an amount corresponding to this rate of "regeneration". The effect of this is that the actual particle utilisation can exceed the limiting value found in the laboratory experiments. It is not, of course, allowed to exceed 1. Corresponding adjustments are made in the calculations of bed composition to allow for size reduction of the particles by abrasion.

Ideally, experimentally determined values of abrasion indices for the various materials and rigs should be inserted into the mathematical model, but since there has not been time to derive them independently, values giving satisfactory agreement have been determined by trial and error.

6. LABORATORY EXPERIMENTAL WORK

6.1 Coal studies (Task VII)

The work carried out to study the release of sulphur from coals is described in detail in Appendix VII.

The experimental work carried out comprised the determination of the various forms of sulphur in coals, cyclone fines from the 36 in combustor and carbonised coal (char) prepared under controlled conditions in the laboratory. The laboratory char was prepared by passing fine coal particles 53 to 75 μm dia, suspended in argon carrier gas through a furnace at 1470°F. The particles were fed and collected by water-cooled probes and the residence time in the furnace was 100 ms. The results obtained are given in Tables 6.1 and 6.2

The ratio of organic to pyritic sulphur is considerably higher in the combustor fines and laboratory char than in the coal. This indicates that the rate of release of pyritic sulphur is generally more rapid than that of organic. A comparison of the sulphur retention for the laboratory char shows that the rates of release of both organic and pyritic sulphur for Welbeck coal are higher than the corresponding rates for Pittsburgh. It is not clear whether this is also the case for the combustor fines because of the large amount of inert material and calcium sulphate in the fines.

For Pittsburgh coal the ratio of organic/pyritic sulphur in the laboratory char is close to that of the cyclone fines, indicating that the pattern of sulphur release is similar. This is not the case for Welbeck coal. Although there were oxidising conditions in the combustor and reducing conditions in the laboratory furnace, it is surprising that there should be agreement for one coal and not for another.

Table 6.1 Forms of sulphur in coals

Coal	Sulphur % as received				Ratio Org./Pyr.
	Total	Organic	Pyritic	Sulphate	
Illinois	3.95	2.45	1.35	0.15	1.8
Pittsburgh	2.75	1.44	1.25	0.06	1.1
Welbeck	1.25	0.73	0.50	0.02	1.4
Park Hill	2.40	1.01	1.35	0.04	0.7

Table 6.2 Forms of sulphur in 36 in combustor fines and laboratory char

Coal	Pittsburgh		Welbeck	
Designation	36 in fines	Lab. char	36 in fines	Lab. char
% sulphur as received				
Total	2.4	2.4	1.3	1.1
Organic	0.3	2.24	0.15	1.06
Pyritic	0.03	0.17	0.06	0.06
Sulphate	2.1	-	1.1	-
% sulphur retention				
Total	-	37	-	30
Organic	-	65	-	54
Pyritic	-	5.4	-	3.6
Ratio: organic/pyritic	10	13	2.5	17.5

6 2 Limestone and dolomite studies

6.2.1 Introduction

The reasons for the differences in the sulphur retention of different stones are generally accepted to be ascribable to differences in physical structure rather than in chemical composition[6,7]. Certainly porosity formation on calcination has been established as an important factor (for example, Potter[6] has found for calcined stones a correlation between pore volume, measured by mercury porosimetry, and their sulphur oxide capacity), although it is not known definitely why various types of stone calcined under the same conditions should give products having markedly different pore structures.

It is clear therefore that basic studies aimed at obtaining further understanding of the retention of sulphur oxides by stones should include measurements of the pore structures of those stones. Such an investigation was carried out in Task VIII and since in the present work stones were fed into the fluidised combustors in the uncalcined state, particular emphasis was placed on following the development of pore structure at various stages of calcination and determining how the pore structure is modified during sulphation.

Quantitative measurements of rates of reaction of SO_2 with the various stones have also been made in order to provide data for use in mathematical modelling of the SO_2 absorption process (Section 5 and Appendix 6).

6.2.2 Pore structure on calcination and sulphation

The main body of the work concerned the use of the mercury injection porosimetry and displacement density methods to follow the development of pore structure on rapidly heating stones and then heat soaking them for various times in chosen atmospheres.

Mercury injection porosimetry is used for determining the distribution of pore volume with respect to pore entrance diameter (p.e.d.). The method depends on the principle that a certain minimum pressure is required to force mercury through an entrance that is not wetted by that liquid; the smaller the p.e.d. the greater is the pressure required. The cumulative volumes of mercury that enter the

the sample as the pressure is increased in steps are determined and the pressures are converted into p.e.d. values by use of a computer program; the curve of cumulative pore volume vs p.e.d. shows the pore volume lying behind entrances with p.e.d. values within any chosen limits in the range of p.e.d. covered. This curve may also be expressed in the first differential form, or as a histogram. In the present work, with an assumption that the pore entrances were circular, the range of p.e.d. covered was 59 μm to 0.014 μm. All the primary cumulative pore volume vs p.e.d. data are collected at the end of Appendix 8.

The displacement density of a solid is the mass of the solid divided by the volume of fluid it displaces on immersion. The further a particular fluid penetrates into the solid the lower will be the displacement volume and the higher the corresponding density. Mercury under 1 atm pressure and helium were used as fluids. The mercury was assumed to penetrate no pores having p.e.d. less than 14.5 μm, and the 'mercury density' was regarded as an approximation to the superficial particle-density of a stone sample. Helium will enter pores with p.e.d. down to 0.26 nm (0.00026 μm); the 'helium density' approximates to the density of the solid matter of stone samples. The reciprocals of the mercury and helium densities give the volume (V_x) of pores with p.e.d. in the range 14.5 μm to 0.26 nm. Porosity values were calculated on a unit weight basis and as percentages of the 'particle' volume (viz, reciprocal of the mercury density).

Exploratory experiments were made in which U.K. dolomite and Limestone 1359 particles were dropped into a furnace at 1470°F to achieve rapid heating and left in the furnace for specified times before removing them for weighing and pore structure examination; the furnace atmosphere was such that either it initially contained air, no attempt at flushing being made, or it was flushed with nitrogen. A further series of experiments on similar lines was carried out with the furnace,at 1470°F or 1650°F, being flushed with a specified gas mixture - composition by volume, 15% CO_2, 3% O_2, 82% N_2,with and without 2000 ppm of SO_2 being present: the residence times of samples in the furnace were ¼, 1 and 4 h;

stones examined were Dolomite 1337, U.K. dolomite, and Limestones 18 and 1359; particle size was -1000 +300 μm. The experiments with SO_2 were intended to simulate the behaviour of stone particles in the combustor. The results have enabled conclusions to be drawn as follows:

(i) The development of porosity[†] on calcination is a time and temperature dependent process; some examples of amounts of porosity formed are shown in Table 6.3.

Table 6.3 Examples of amounts of porosity (V_x, % v/v) formed in stones on calcination*, and the extents of calcination** (in brackets)

Stone	Raw Stone	Temperature and time of calcination			
		1470°F		1650°F	
		1/4h	4h	1/4h	4h
Dolomite 1337	8	24 (34)	33 (52)	52 (85)	54 (90)
U.K. dolomite	5	33 (57)	41 (69)	54 (96)	56 (100)
Limestone 18	7	14 (15)	17 (30)	45 (85)	48 (96)
Limestone 1359	2	5 (4)	14 (19)	44 (86)	46 (91)

* Using the gas mixture 15% CO_2, 3% O_2, 82% N_2, zero SO_2.

** Weight loss expressed as a percentage of weight loss for complete calcination.

The amount of porosity (% v/v) formed is for each stone a linear function of CO_2 loss.

(ii) On calcination, porosity is generated initially much more rapidly in dolomite than in limestone (see Table 6.3). This difference is most marked in a CO_2 bearing atmosphere at 1470°F. The effect is evidently associated with the decomposition of the $MgCO_3$ in dolomite.

(iii) There is little, if any, porosity with p.e.d. in the range 0.014 μm to 0.26 nm, with the calcined-only materials or, with the possible exception of Limestone 1359, with the calcined-sulphated ones.

[†] The term porosity herein means V_x, unless otherwise stated.

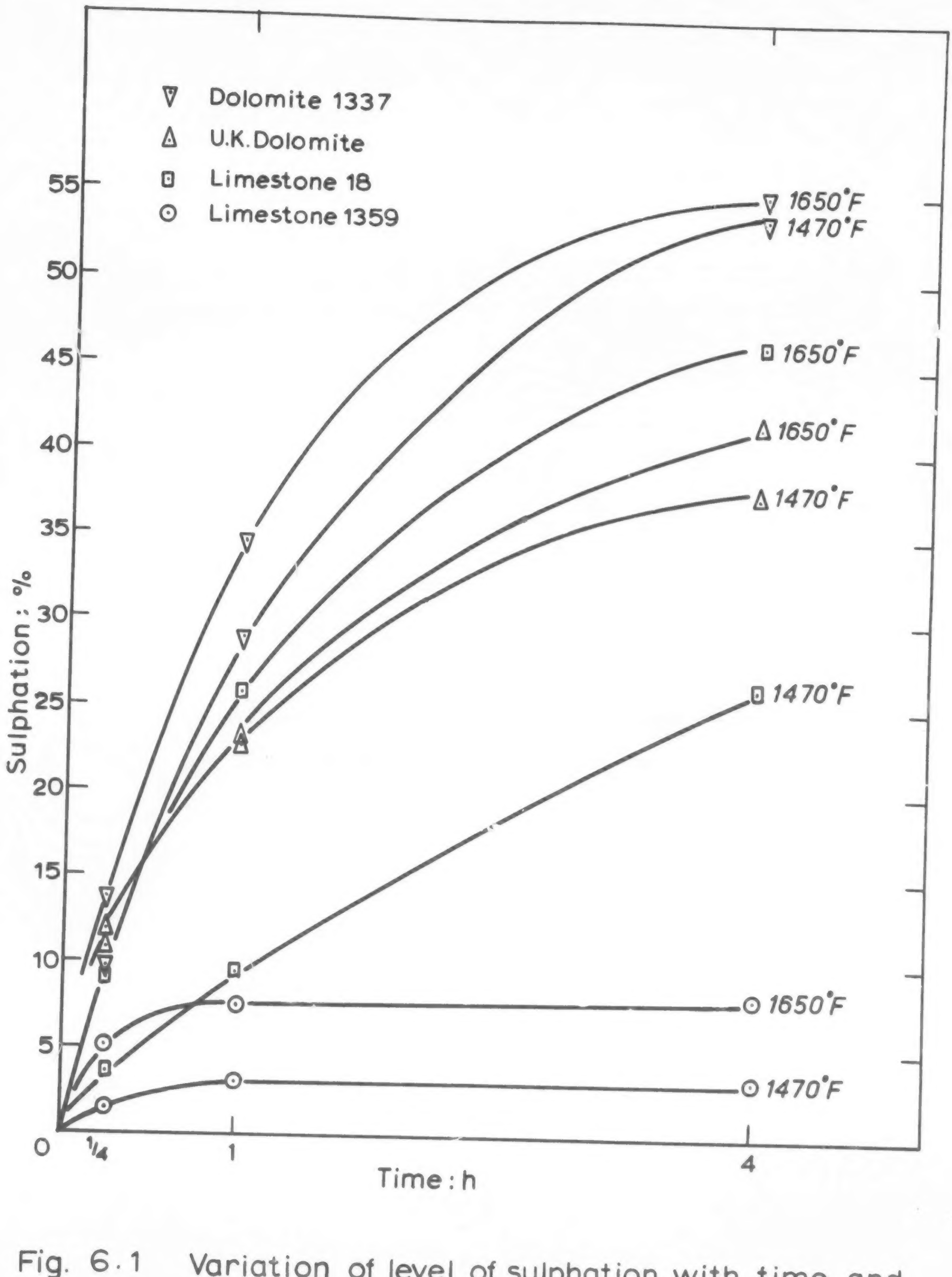

Fig. 6.1 Variation of level of sulphation with time and temperature

(iv) Sulphation* varies with time, as shown in Fig. 6.1. It is emphasised that the stones were not precalcined before being exposed to SO_2

(v) Sulphation caused a reduction in porosity. It was found that sulphur is accommodated in the smallest pores (as detected by the mercury porosimetry) in the stone, e.g. with Dolomite 1337 at 1650°F most of the porosity filled, blocked off, otherwise eliminated on sulphation lay in pores with p.e.d. between 0.1 μm and 0.03 μm; with Limestone 18, part of the sulphation took place in pores with p.e.d. between 0.3 μm to 0.1 μm.

(vi) As the results in Fig. 6.1 clearly show, Limestone 1359 is poor compared with the other stones in its ability to absorb SO_2. The studies of calcination showed that, of the stones, Limestone 1359 is the poorest in quantity of relatively large pores (say, with p.e.d. in the range 14.5 μm to 0.3 μm) whose presence would facilitate the more rapid ingress of SO_2 to the interior of the particle and lead to more rapid reaction. Contrawise, Limestone 18 shows the most pronounced development of pores in this range of p.e.d. On sulphation the volume of pores with p.e.d. $>$ 0.3 μm shows little change with the two dolomites, viz, the 'transport pores' retain their identity, but with Limestone 18 progressive reduction in the volume of these pores occurs as the level of sulphation increases. As comparison of the results in Table 6.3 with those in Fig. 6.1 shows, the level of sulphation reached under the present conditions does not depend solely on the amount of porosity developed in the stone on calcination alone. A fairly high porosity is developed in Limestone 1359 after 4 h at 1650°F but the level of sulphation remains relatively low (evidently owing to the lack of transport pores, as mentioned above) and indeed the porosity in the stone after 4 h at 1650°F in the SO_2 bearing atmosphere is as much as 42%. Comparison of the latter with the mercury porosimetry data suggests that the sulphation may have caused narrowing of some pore entrances to $<$0.014 μm diameter (cf., 6.2.3 below).

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* Sulphation is defined here as the ratio of the quantity of sulphur taken up by the sample to that taken up if all the CaO were converted to $CaSO_4$.

(vii) It appears that at least two criteria of pore structure have to be met if a stone is to be a good SO_2 absorber:

- (a) extensive volume as large, viz, transport, pores for ease of access to the interior of the stone;
- (b) extensive volume, for accommodation of the sulphur, as relatively small pores - which have a higher surface/volume ratio than larger pores.

In the case where one factor is missing, as in Limestone 1359 with little porosity in large pores, or, in Potter's work,[6] with Iceland Spar containing low porosity, then the sulphur uptake is liable to be poor.

(viii) The mechanism of sulphur fixation is not clear but some points arise from the present work:

(a) Since sulphur is found in the smallest pores the SO_2 probably does not react to sulphate at the point of first contact with the stone, in which case the SO_2 must migrate in some form until a certain favourable site or condition is obtained.

(b) Increasing the temperature from 1470° to 1650°F does not cause the increase in rate of sulphation with the dolomites that might be expected from chemical kinetics considerations. This effect may be related to the observation in the pilot plant work that the efficiency of removal of SO_2 passes through a maximum at about 1560°F.

(c) With dolomites, at least, a highly speculative suggestion, based on the observation made during the course of the work (see Section 6.2.4 below) that the last traces of water were difficult to remove, is that an oxygen-containing species, perhaps hydroxide, localised on the internal surface of the stone is necessary in the formation of the sulphate; increase of temperature above a certain level could cause such a surface species to become mobile resulting in reduced formation of sulphate.

The chemistry of the sulphur retention process, and the possible influence of water on this and on the formation of the pore structure itself, would seem to be worthy of further study, particularly as such work may lead to an understanding of the mechanism, and hence perhaps elimination of, the fall-off in sulphur retention above about 1560°F referred to above.

6.2.3 'Impermeable layer' formation on sulphation

It has been possible to demonstrate the presence of an impermeable' layer or 'shell' within the particles of a sample of Limestone 1359, sulphated in the laboratory using the method briefly described in 6.2.9 This was not found within Limestone 1359, sulphated in a combustor, nor within sulphated samples of Dolomite 1337 and the U.K. dolomite.

The method used was as follows:

(i) Mercury porosimetry curves of the sulphated stones were measured.

(ii) Further samples of the sulphated stones were taken and the particles broken individually using a razor blade; the product was then sieved to remove particles smaller than 300 μm and the porosimetry curves of the +300 μm particles were measured.

The porosimetry curves for the Limestone 1359 sulphated in the laboratory show that there is considerably porosity within the whole sulphated particles not reached by mercury in the porosimeter but that some or all of this porosity is made accessible on simple cleavage of the particles.

No such increase of accessible porosity was seen with a Limestone 1359 sample that was calcined but not sulphated, nor with the plant-sulphated stone or the sulphated dolomites. Evidently in the laboratory-sulphation of Limestone 1359 some pore entrances have been narrowed to <0.014 μm diameter; the presence of such narrowed entrances, which may be regarded as a form of 'shell', will aggravate the poor sulphation behaviour of the stone. Such 'shell' formation is presumably associated with the less open pore structure in this stone in comparison with the dolomites which do not show the effect. It is possible that with the plant-sulphated Limestone 1359, a 'shell' was destroyed, or was prevented from forming, by attrition in the fluidised bed.

6.2.4 Porosity at elevated temperature

It is known that certain materials such as glasses and synthetic graphites contain pores with entrances through which a particular gas molecule will pass at one temperature but not at another, viz, accessibility of pores to gases may change with temperature. Usually, with increase of temperature, accessibility would increase ('closed-pore penetration'), the extent of the effect being related to the molecular size of the gas, but a decrease has been observed ('open-pore closure').

As pore structure measurements, in general, and on stones in particular, have in the past been made at room temperature or lower, it was considered necessary in the present work to investigate the extent of any change in the accessibility to relevant gases of pores in stones when the temperature is increased to combustor temperature.

The methods used to detect either type of accessibility change depend on the principle that gas that penetrates a pore at a particular temperature becomes trapped in the pore when the temperature is changed to that at which the pore is no longer accessible to the gas. After removal by evacuation of the free gas, the trapped gas may be released for measurement by bringing the temperature of the solid back to the original temperature of penetration.

The U.K. dolomite and Limestone 1359 were examined in the temperature range, room temperature to 1470°F. The principle limitation of the work is that all the samples examined, which included some from the exploratory experiments mentioned in 6.2.2, became perforcefully calcined in vacuum before the experiments were started.

Four inert probe-gases were used, of increasing molecular size: helium, neon, krypton and xenon, the last being similar to SO_2 in molecular diameter. Gas release was measured using a mass spectrometer.

With both stones there was no open-pore closure effect with any of the gases nor any closed pore penetration by helium or neon. Large apparent closed pore penetration effects by xenon were observed with some samples of both stones, but with the dolomite and probably the limestone, the effects were largely due to residual adsorption at room temperature of xenon in open fine pores, this gas not being pumped away with the free gas and subsequently appearing on increasing the temperature along with any released from previously inaccessible pores. But the total times taken for the xenon to be released at 1470°F in vacuum were between 10h and 100h and it is expected that any contribution of xenon due to closed-pore penetration would have been released more slowly than that merely residually adsorbed: this is taken to mean that the penetration of any closed pores is a slow process compared with the rate of sulphur uptake by the stone and is likely to be of only secondary importance, if at all, in the combustor. Apparent closed-pore penetration effects were also observed with krypton, but these were much smaller than, and analogous to, those with xenon.

There were some qualitative differences in quantity of residually adsorbed xenon released between the -1000 +300 μm dolomite and limestone samples, presumably reflecting corresponding differences in open fine-pore structure. The results are difficult to interpret, however, and are influenced by calcination history which varied among the samples; attention has been called to the differences because of the other differences that have been observed between the stones, for example, in SO_2 sorption capability.

Finally, the following incidental observations were made during the course of the experiments.

(a) Traces of 'water' were retained by the U.K. dolomite samples, but not by the limestone ones, for extensive times at 1470°F under reduced pressure. This water is presumed to have been combined as $Mg(OH)_2$, the last vestiges of which were difficult to decompose.

(b) SO_2 was released from the U.K. dolomite in vacuum on increasing the temperature from 1470° to 1650°F; the quantity of SO_2 originally present in the material was estimated from this to be <15 ppm (w/w). Although this is a very small quantity, the observation may have some significance, possibly in the problem of the reduction in SO_2 uptake on increasing the temperature in the combustor to above 1560°F.

6.2.5 Effect of thermal cycling on SO_2 uptake

Elutriated stone fines are subjected, if recycled, to rapid temperature changes and it has been suggested that such 'thermal cycling' might have an effect on the capability of the recycled fines for absorbing SO_2. Experiments were designed to test this possibility.

The sulphur retentions of thermal cycled and non-cycled samples were compared. The two samples were sulphated simultaneously with both samples in the same furnace: one sample was taken through a thermal cycle experiment whilst the other was maintained in the hot region at constant temperature. In this way it was intended that only the effect of the thermal cycling should be apparent and possible differences that might have arisen between separate experiments, for example, due to variability in gas flow, avoided.

-1000 +300 μm and - 53 μm samples of the U.K. dolomite and Limestone 1359 were used, with four gas-flow compositions: SO_2, 1500 to 10000 ppm; CO_2, 0 to 75%; O_2, 2 to 10%, all v/v. The furnace temperature was 1470°F. The cyclic temperature changes were not seen to have any systematic effect on the sulphur retention of the limestone or the dolomite.

Incidental observations made in the course of these experiments were:

(a) Change of particle size of the stone from -1000 +300 μm to -53 μm resulted in an increase in sulphur uptake for all of the atmospheres used; the effect was larger with the limestone.

(b) Increase of the CO_2 concentration to 75% caused a substantial decrease in the SO_2 uptake with both stones and both particle sizes. With -1000 +300 μm material the effect was much more marked with the limestone.

(c) Overall, under the conditions of the experiments, in the -1000 +300 μm size grade, the dolomite is the better SO_2-absorber. As expected, reducing the particle size to -53 μm appears to largely eliminate the difference in SO_2 uptake between the two stones, particularly at the CO_2 concentration of 75%.

6.2.6 Deposition on U.K. dolomite

A brief optical microscopical examination was carried out on U.K. dolomite particles from the bed of the pressurised combustor, after completion of Test Series 1. The major portion of ash was first removed with a magnet and the -300 μm dolomite particles were examined. Generally, they were covered with a shell of fused brown deposit; some of them were chipped or broken and in others the shell apparently had become detached from the particle. The shell is presumably a slag formed with ash in the combustor: no such shell was observed on the samples prepared in the laboratory. No comment can be made on the role of the shell in the sulphation process.

6.2.7 Surface area

A few measurements of surface area, using the BET method, were made in the course of the work.

6.2.8 A simple test for stones

The most simple and satisfactory laboratory-method of placing unknown stones in order of acceptor ability would seem to be a sulphation experiment wherein stone particles are dropped into a tube at reactor temperature through which an appropriate SO_2 bearing gas stream flows (see 6.2.2). Subsequent analysis for Ca, CO_2 and SO_2 content would enable curves to be constructed showing the variation of the level of sulphation with time (cf. Fig. 6.1).

6.2.9 Reaction rate measurements

Measurements were made on Dolomite 1337, the U.K. dolomite and Limestones 18 and 1359 to obtain data on reaction rates specifically for use in mathematical modelling of the SO_2 absorption process. The reaction rate constant was derived as a function of sulphation, particle size and temperature.

The materials used were taken from the uncrushed material supplied for the plant experiments. These were crushed in the laboratory and size graded for the reactivity experiments.

Mixtures of O_2, N_2, CO_2 and SO_2 in various proportions (constant for each experiment) were passed through a thin bed of the stone, and the amount of SO_2 absorbed by the stone was determined after the lapse of successive intervals of time. The amount of SO_2 absorbed was determined from the absorption of the residual SO_2, in the gas stream after passage through the bed, in hydrogen peroxide solution and titration with standard alkali. The experiments were repeated at different temperatures and using different particle sizes.

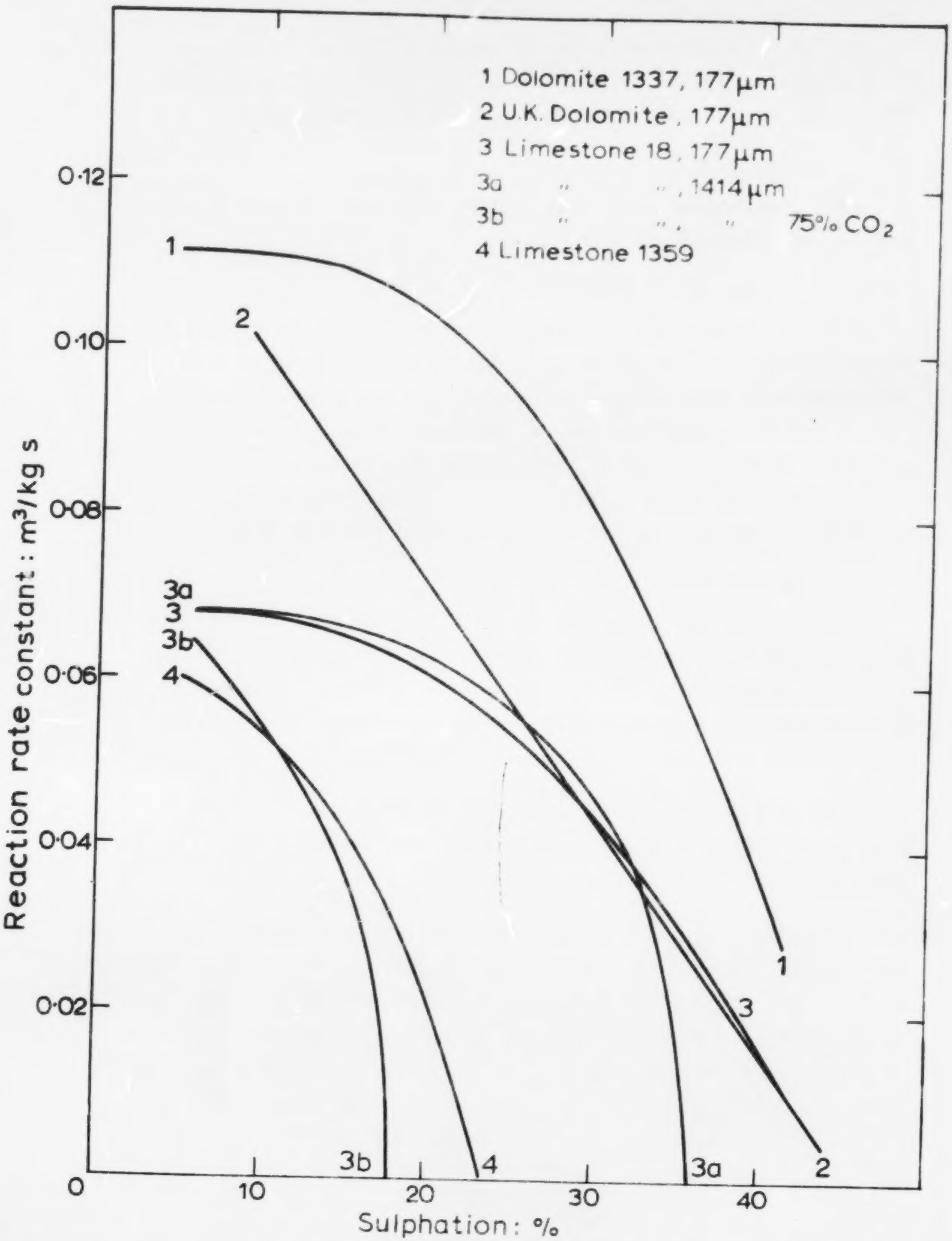


Fig. 6·2 Comparison of reaction rate constants of different stones

The choice of a static bed for the experiments was governed by the need to ensure that the SO_2 concentration change through the bed was as small as possible, in order to simplify interpretation of the results. This necessitates use of a thin bed, and hence rules out the possibility of using a fluidised bed.

Argonne National Laboratory have found in previous work[8] that over the range of gas velocities likely to be encountered in fluidised combustion beds, the reaction rate between stone and SO_2 is substantially independent of gas velocity. In the present work, velocities were kept as close as possible to those used in the plants, thus reducing as far as possible any errors due to dependency of reaction rate upon mass transfer of SO_2 to the particle surface.

Reaction rate constants are expressed in units of m^3/kgs. This is a rate of mass of SO_2 absorbed per unit mass of stone per unit of SO_2 concentration expressed in mass per unit volume, i.e., kg SO_2 absorbed per kg stone per second per (kg $SO_2 \div m^3$ gas mixture).

The results showed that the reaction rate constants of the four stones at zero sulphation did not differ widely either with stone type, with particle size, with CO_2 concentration, or with temperature, generally lying in the range 0.05 to 0.1 m^3/kgs, the limestones lying near the bottom and the dolomites near the top of this range. At sulphations greater than 10%, however, there is considerable variation in rate between different stones, between different particle sizes, and with temperature and CO_2 concentration.

Fig. 6.2 illustrates a few of the results. Curves of rate constant vs sulphation are shown for 177 μm particles of the four stones, in $O_2/N_2/SO_2$ mixtures at 1470°F, together with curves for larger particles (1414 μm) of Limestone 18 in air/SO_2 mixtures and $O_2/N_2/CO_2/SO_2$ mixtures at partial pressures of CO_2 in the neighbourhood of those obtaining in combustion at 5 atm pressure.

The results show the reactivity of the various stones to be consistent with their behaviour in the 'drop-tube' experiments referred to earlier (6.2.2 and 6.2.8) and show that the latter method is suitable for a simple assessment of the efficiency of a stone in retaining sulphur in the bed.

7. DISCUSSION

7.1 Emission of SO_2

7.1.1 Introduction

The main finding of all the experimental work described in this report is that it is technically feasible to reduce the SO_2 emission from coal-fired fluid-bed combustors to the levels required by existing ordinances or likely future legislation by injecting into the bed sufficient lime in the form of limestone or dolomite.

The effect on SO_2 emission of changing operating conditions is discussed under the following headings:

(a) Calcium to sulphur ratio
(b) Combustion temperature
(c) Fluidising velocity
(d) Bed height
(e) Operating pressure
(f) Fines recycle
(g) Particle size
(h) Additive type
(i) Coal type

The process data were obtained from five combustors. Consequently, before commenting on the effects of the variables, the extent to which the data may be considered to be homogeneous is examined. The time taken to reach steady operating conditions and the mathematical model are discussed at the end of the section.

The accuracy of the data obtained is also discussed later (section 7.1.13). The reproducibility of the SO_2 emission in replicate tests was found to be ± 29% of the value. For a coal with 3% sulphur (Pittsburgh) this leads to reproducibilities of percentage SO_2 reduction of, for example ± 15% at 50% SO_2 reduction and ± 5% at 85% reduction. Differences between single results within these limits may not be significant, but smaller differences between sets of results, e.g. curves through a number of points, are meaningful.

7.1.2 Effect of plant design

The main differences between the five pilot-plants can be summarised as follows:

(i) Bed cross-section: This ranged from about 0.2 ft^2 to 8 ft^2. Two were circular, two rectangular and one was square.

(ii) Cooling surfaces in the bed: These ranged from closely packed banks of 1 in outside diameter tubes extending over almost the whole height of the bed (48 in x 24 in pressurised combustor), to widely spaced 2.37 in outside diameter tubes extending over only a part of the bed height in the 36 in combustor. In the pressure combustor there were several rows of tubes at and immediately above the bed surfaces to minimise splashing and carryover.

(iii) Cooling of the freeboard: Excessively high temperature in the freeboard was prevented by direct steam-injection in the 36 in combustor, by cooling coils in the pressure combustor and by water cooled walls in the 27 in combustor. In the 6 in combustor the freeboard was heated to avoid the temperature dropping below the bed temperature.

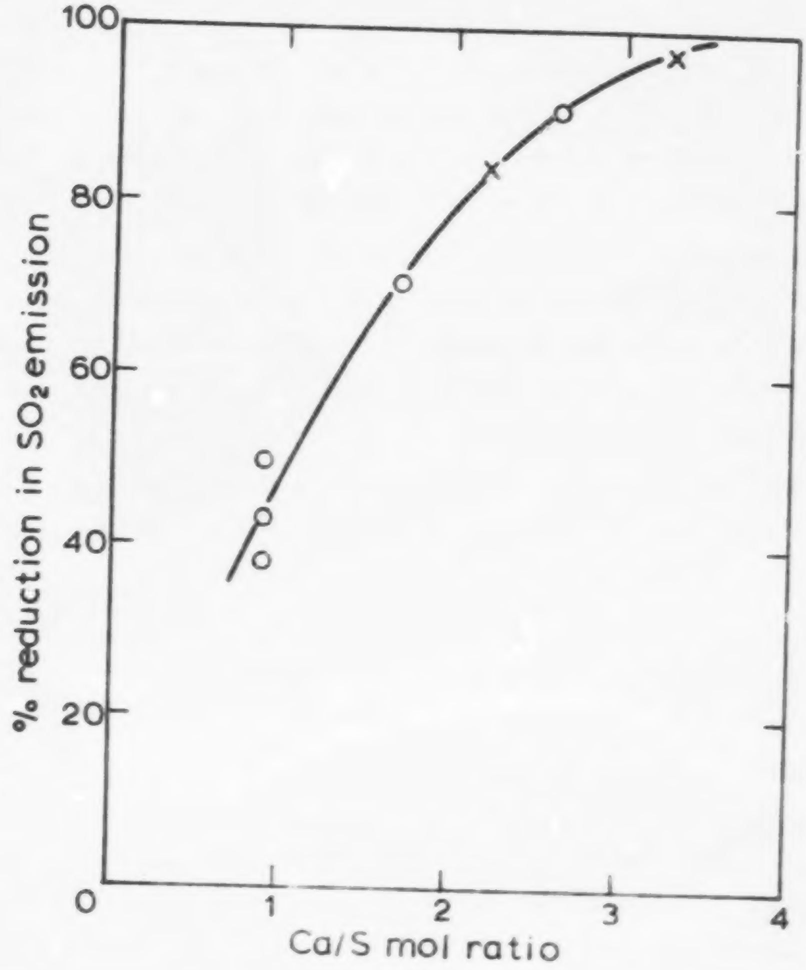
(iv) Feeding of additive: Additive was fed through a single nozzle separately from the coal feed in the 36 in combustor but in the others it was premixed upstream of the coal feed point.

(v) Feeding of coal: The area of bed served by each coal feed nozzle in the large combustors ranged from 2 ft^2 for the pressure combustor to 4 - 4½ ft^2 for the 27 in and 36 in combustors.

(vi) Operating pressure and velocity: The 48 in x 24 in pressurised combustor, the 12 in combustor, and the 6 in combustor, were only equipped to operate at low velocities (3 ft/s or lower). Observations on the effect of higher velocities depend upon the results from the 27 in and 36 in combustors. Operation under pressure was of course restricted to the 48 in x 24 in combustor

(vii) Recycle of carryover material: The 36 in combustor was equipped with an external fines recycle system. The 27 in combustor had both internal and external systems: the internal system was in use at all times and reference in the remainder of the report to operation without recycle refers only to the external system. The other combustors had only internal and hence less positive recycle systems.

The performances of the combustors under closely similar operating conditions have been compared in Figs. 7.1, 7.2 and 7.3 by plotting the percentage reduction in SO_2 against the Ca/S mol ratio. The main comparison was between the 36 in and the 6 in combustors, and Fig. 7.1 shows that their performances are identical. The performance of the 27 in combustor (Fig. 7.2) is slightly better than that of the 36 in combustor, probably because of the internal fines recycle in the 27 in rig. Comparison between the performances



Pittsburgh coal
Limestone 18 (−1680μm)
Bed depth 2ft
Fluidising velocity 3ft/s
Bed temperature 1470°F
No recycle
o 6in combustor
x 36in combustor

Fig. 7.1. Comparison of SO_2 reduction in 6in and 36in Combustors

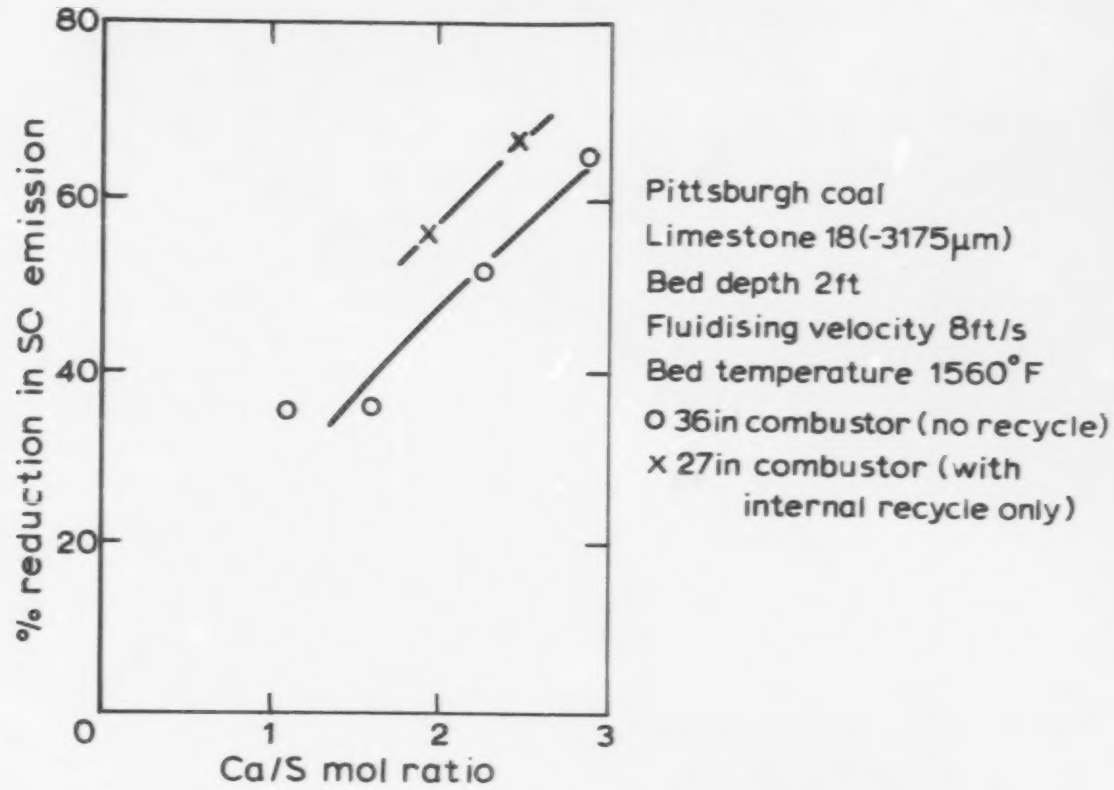


Fig. 7.2. Comparison of SO_2 reduction in 27in and 36in Combustors

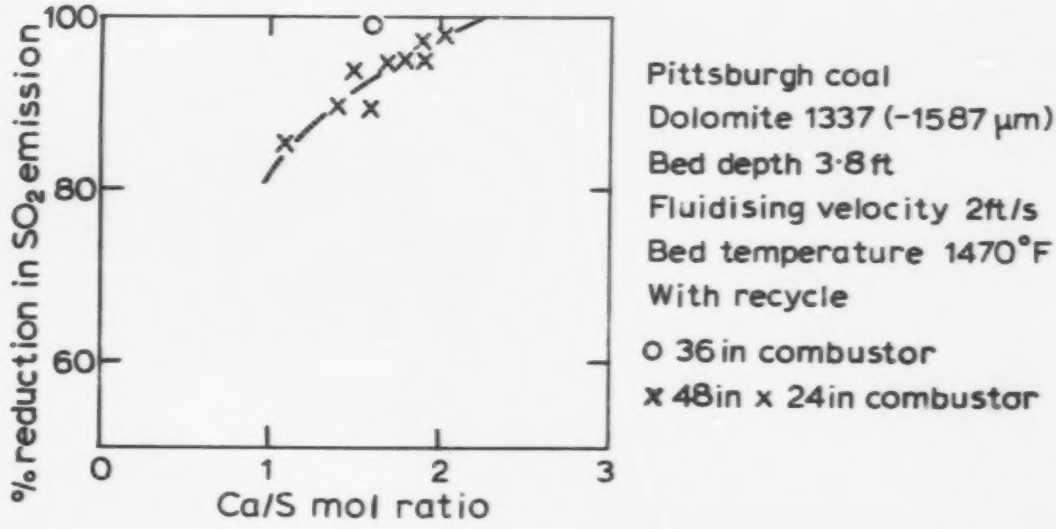


Fig. 7.3. Comparison of SO_2 reduction in 36in and 48in X 24in Combustors

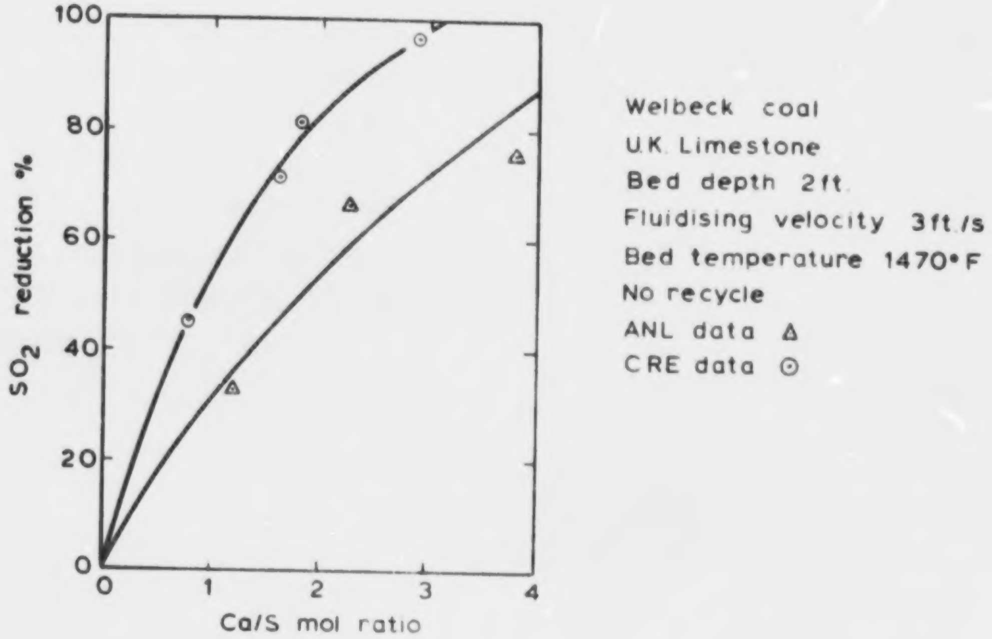


Fig 7.4 Comparison of performance of the 6in. combustors at CRE and ANL

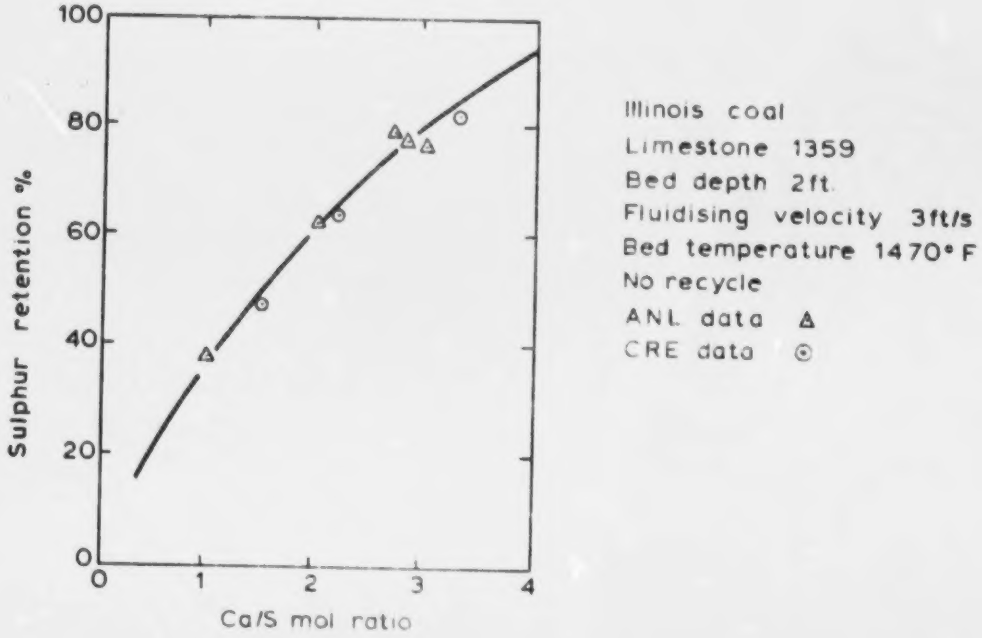


Fig 7.5 Comparison of performance of the 6in combustors at CRE and ANL

of the 36 in and 48 in x 24 in combustors with recycle. Fig. 7.3, shows the SO_2 reduction in the former to be slightly more efficient, but the difference could be accounted for by the more effective recycling system of the 36 in combustor.

At the outset of the programme it was thought that the differences between the sulphur retention performances of the 6 in combustors at the CRE and the Argonne National Laboratories might be due to differences in design (Table 7.1). When burning Welbeck coal (1.6% sulphur d.a.f.) the sulphur retention at the ANL was appreciably lower than that obtained at the CRE (Fig. 7.4). It was found, however, that sulphur retentions obtained in the two combustors when burning high sulphur Illinois coal were in close agreement (Fig. 7.5), and it was concluded that the design differences were unlikely to cause differences in sulphur retention.

Although it can be concluded that design differences between the pilot scale combustors did not affect SO_2 reduction, direct application of the present results to full scale requires some caution. Departure from certain features of the rigs in scaling-up could lead to significant differences in performance. For example, increasing the area served by a coal feed point might result in inferior performance, as suggested by the twofold differences in SO_2 concentration found over the cross section of the 36 in combustor. The effects of other design factors are discussed later.

Table 7.1 Design differences between CRE and ANL 6 in Combustors

	CRE	ANL
Dia. of upper part of freeboard	17 in	6 in
Cooling	Internal water coil	External
Air distributor	Drilled plate	Bubble cap
Insulation of freeboard	Yes	No
Coal and additive feeds	Premixed	Separate
Air preheat temperature	Not preheated	850^oF
Method of SO_2 Determination	Wet methods (H_2O_2 and iodine)	Infra red analyser

7.1.3 The effect of Ca/S ratio

As would be expected, and as predicted by the mathematical model, the percentage reduction in SO_2 emission increases with increase in the Ca/S mol ratio. Sections 4.1, 4.2, 4.3 and 4.5 contain several plots showing the variations of percentage reduction with Ca/S mol ratio, and many of the curves show that the SO_2 emission can be reduced to very low levels. The Ca/S ratio is the most significant operating variable determining the reduction in SO_2 emission, and it would have been useful to have a correlation of the percentage reduction with

Ca/S ratio. The mathematical model gives little guidance on the form of a possible correlation, since it does not compute the percentage reduction analytically but by an iterative method.

Examination of the curves of percentage reduction vs Ca/S ratio suggests that there is an approximately exponential relationship of the form $R = 100\ (1 - \exp(-MC))$ where R is percentage SO_2 reduction, C is the Ca/S mol ratio and M is a constant depending on coal, additive and operating conditions. Detailed analysis of the results suggests that some of the curves do not fit the exponential relationship well, possibly because of anomalies introduced by effects of particle residence time, attrition, etc., or, as in the mathematical model, by the SO_2 release profile in the bed. The exponential relationship has therefore been used only for small extrapolations of data to permit comparisons to be made at a common Ca/S ratio.

An indication of the quantities of additive required to meet the target levels of SO_2 emission expected for (a) built-up areas (300 ppm) and (b) some densely populated areas in the U.S. (100 ppm) is given in Table 7.2. The quantities are for a combustor operated under the optimum conditions of temperature, with a low fluidising velocity and with fines recycle. The stoichiometric requirements for calcium carbonate are 3.15 lb/lb of sulphur, and for dolomite 5.75 lb/lb of sulphur.

Table 7.2 Additive requirements for a 100 MW power plant boiler (900 short tons/day of 3% Sulphur Coal)

Quantity required	Target level of emission ppm v/v	
	300	100
1. Ca/S ratio	1.1	1.8
2. Weight of additive/lb S removed		
(i) Limestone lb	4.1	5.9
(ii) Dolomite lb	7.6	10.8
3. Quantity of additive required		
(i) Limestone ton/day	110	160
(ii) Dolomite ton/day	180	280
4. Quantity of sulphated additive to be disposed of		
(i) Limestone ton/day	110	150
(ii) Dolomite ton/day	150	210

7.1.4 The Effect of Combustion Temperature

It was found in laboratory studies of additive reactivity that the rate of reaction of additive with SO_2 increased with temperature up to about 1650°F, but the variation was not in accordance with the manner expected from the Arrhenius relationship. The results of pilot-plant studies of the effect of combustion temperature on the reduction in SO_2 emission are shown in Figs. 7.6 and 7.7. Data interpolated from these curves together with those from other comparisons, are summarised in Table 7.3. They show that for both limestone and dolomite there appears to be an optimum temperature for removal of SO_2 in the range 1400 to 1600°F. The shape and temperature of the peak is not consistent. This may be the consequence of experimental errors associated with the few data at widely spaced temperatures or may be a real effect resulting from the influence of other operating variables. For example, it is known from laboratory studies of Limestone 18 that the reaction rate constant varies with temperature in a manner that depends on the fraction of lime utilised (Fig. 7.28). With fresh lime (less than 20% converted) the reaction rate constant continues to rise with increase in temperature up to at least 1650°F, but as the fraction of lime reacted increases, a peak develops in the curve, and becomes progressively more

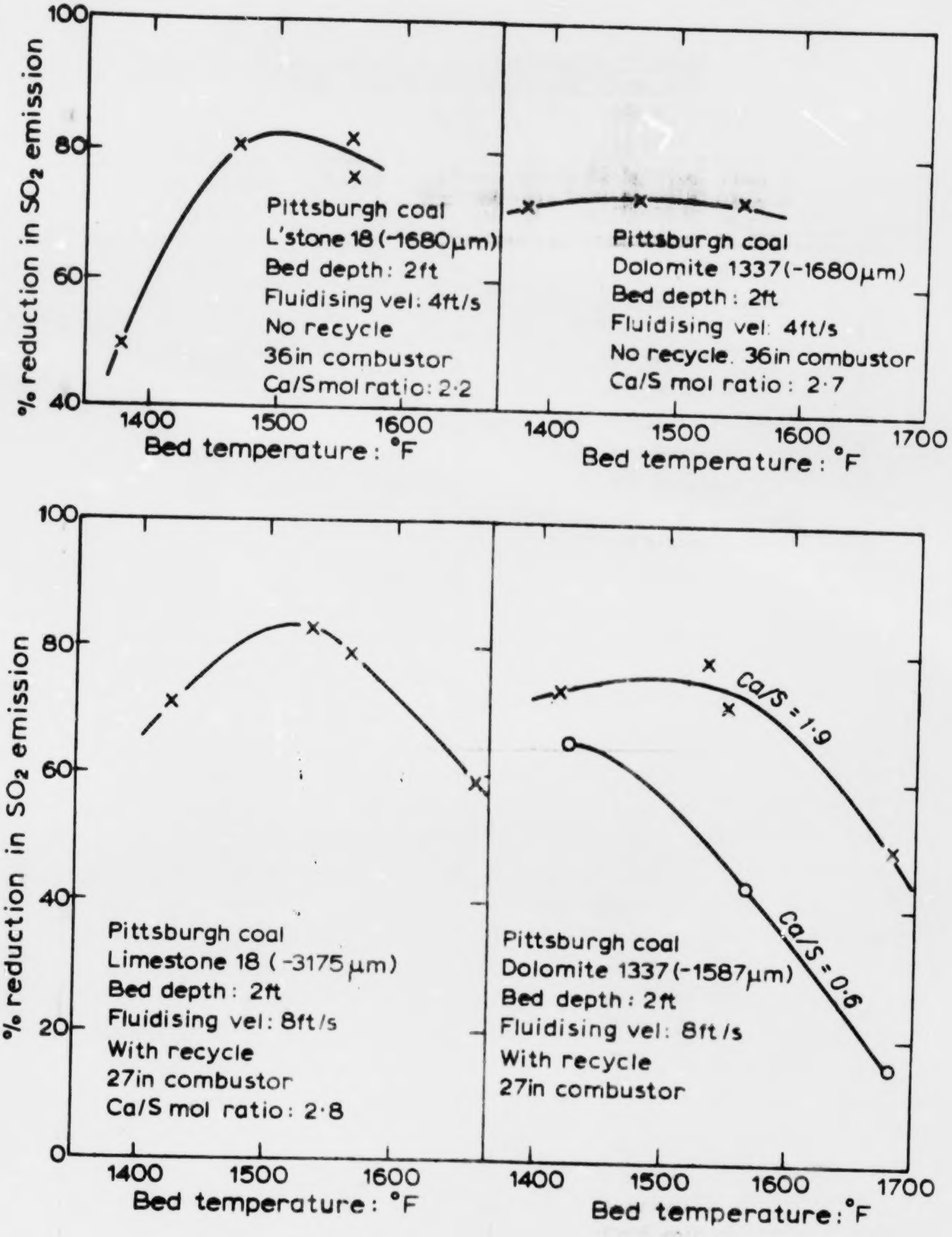
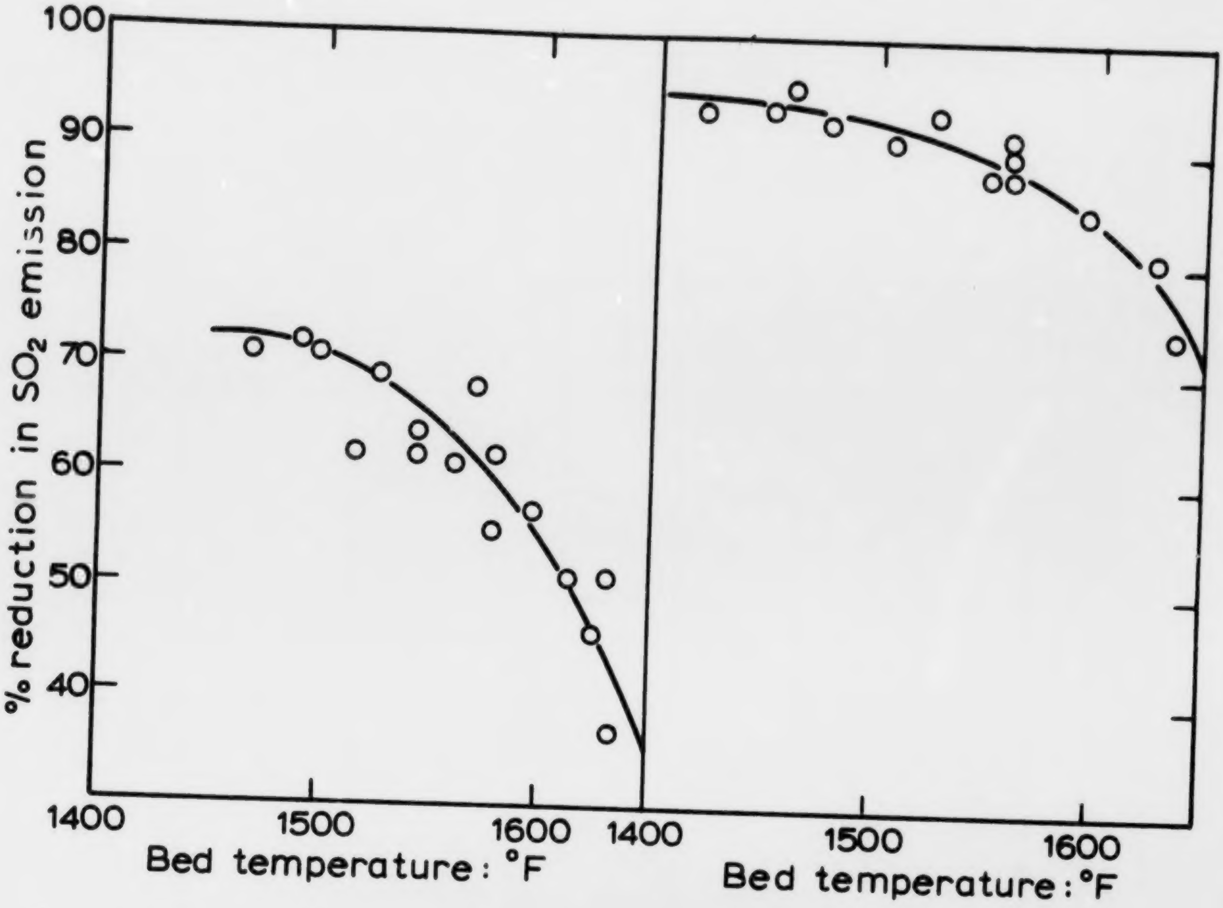


Fig. 7.6. Effect of bed temperature on SO_2 reduction



Welbeck coal
U.K. Limestone (-3175 μm)
Bed depth: 2ft
Fluidising velocity: 8ft/s
Ca/S mol ratio: 2·8
No recycle
36in combustor

Pittsburgh coal
Dolomite 1337 (-3175 μm)
Bed depth: 4ft
Fluidising velocity: 8ft/s
Ca/S mol ratio: 5·3
No recycle
36in combustor

Fig. 7. 7. Variation of SO_2 reduction in temperature surveys

Table 7.3 Effect of Combustion Temperature on Reduction in SO_2 Emission

Coal and Top size µm	Additive and Top size µm	Task	Nominal Bed Ht. ft.	Nominal Velocity ft/s	Recycle	Ca/S mol Ratio	% Reduction in SO_2 Emission at:				
							1290°F	1380°F	1470°F	1560°F	1650°F
Pittsburgh 1680	Limestone 18 1680	I	2	4	No	2.2	-	50	81	79	-
Pittsburgh 3175	Limestone 18 3175	III	2	8	Yes	2.8	-	-	81*	80*	62*
Illinois 1680	Limestone 1359 1680	V	2	3	No	2.2	19	-	64	-	-
Welbeck 3175	UK Limestone 3175	I	2	8	No	2.8	-	-	72**	64**	36**
Pittsburgh 1680	Dolomite 1337 1680	I	2	4	No	2.7	-	72	74	73	-
Pittsburgh 3175	Dolomite 1337 1587	III	2	8	Yes	0.5	-	-	61*	45*	22*
					Yes	1.9	-	-	76*	74*	57*
					No	4.8	-	-	-	77	64
Pittsburgh 3175	Dolomite 1337 3175	I	4	8	No	5.3	-	95**	94**	89**	72**

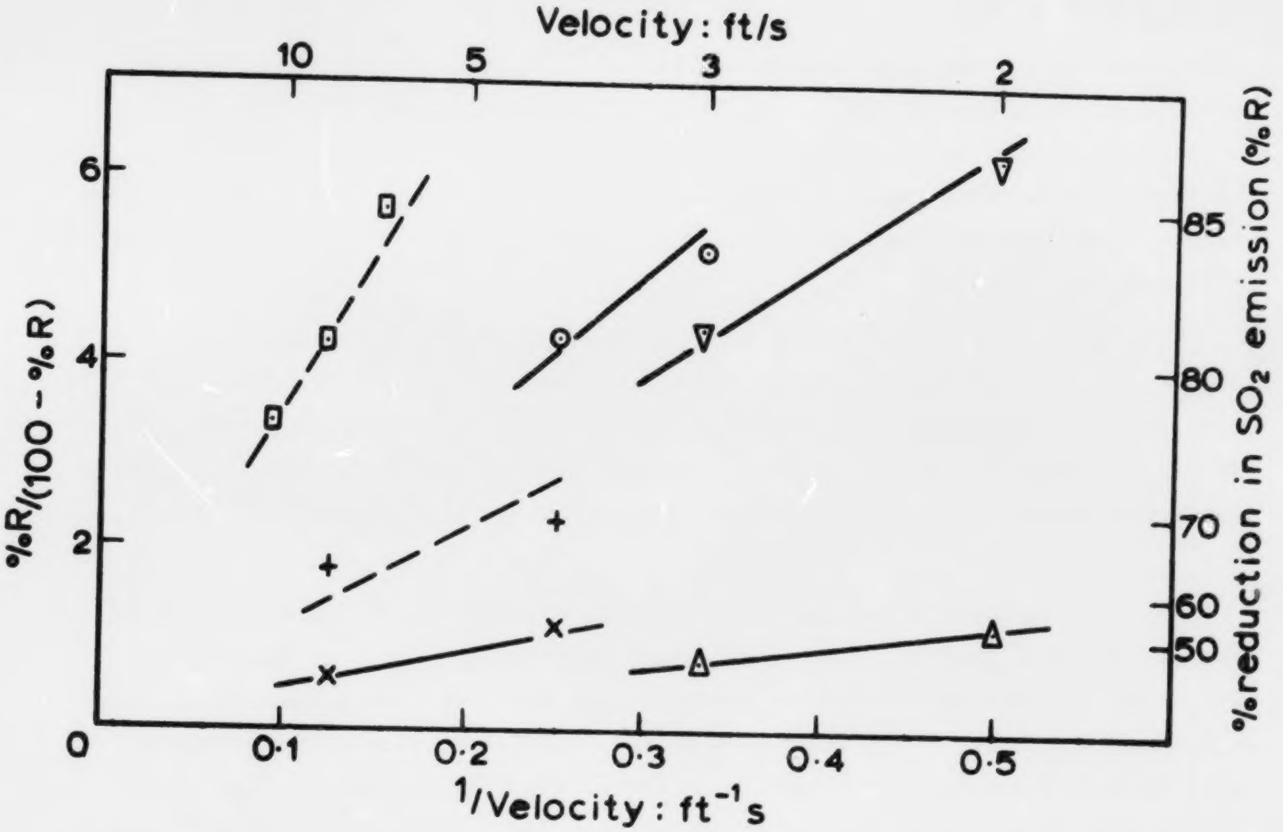
* Interpolated from plotted data (Fig. 7.6)

** Interpolated from temperature surveys (Fig. 7.7) pronounced whilst the peak temperature falls. If this behaviour occurs under combustion conditions in the plant, it could be expected that the shape and temperature of the peaks in the curves shown in Figs. 7.6 and 7.7 would depend on factors (e.g. Ca/S ratio, fluidising velocity, bed height, recycling, particle size, additive and coal characteristics) that influence the fraction of lime utilised.

It is known that calcium sulphate decomposes at temperatures above $1900^{\circ}F$, but the existence of optimum temperatures below $1600^{\circ}F$ was unexpected both from the laboratory work and from the good retention performance obtained by Zielke, Lebowitz, Struck & Gorin[illegible] working at $1800^{\circ}F$ with dolomite. It is confirmed however by the behaviour of limestone found by Esso Research Engineering Co.[10]

The explanation may be in the factors that affect the conversion of the initial reaction product, $CaSO_3$ (unstable), into $CaSO_4$. If, for example, hydroxide ions are involved it is possible that there will be a temperature above which the stability of hydroxide ions on the internal surface of the particles will decrease, and hence the nett retention of SO_2 will be lower. The possibility of hydroxide ions being present was demonstrated in the pore structure studies (Appendix 8, Section 2.4.2.8)

Reduction of temperature below the optimum ultimately results in a major increase in sulphur emission when limestone is the additive, whereas the effect with dolomite is small. When limestone is used, reaction is largely governed by the temperature-dependent rate of the calcination reaction which develops pores for penetration by SO_2 and internal surfaces for reaction. It is probably this factor that gives limestone a more clearly defined optimum temperature range than dolomite; The $MgCO_3$ in dolomite calcines at a lower temperature than $CaCO_3$ and hence gives access to internal surfaces that would otherwise be masked by an impermeable layer of $CaSO_4$. The higher SO_2 emission with limestone at low temperature could limit reduction of load by reduction of temperature. The critical and possibly anomalous effects of temperature on sulphur emission warrant careful consideration in any future work.



Symbol	Coal	Additive	Size µm	Bed depth ft	Bed temp. °F	Ca/S mol ratio
×	Pittsburgh	18	3175	2	1560	1·7
○	"	"	1680	2	1470	2·2
Δ	Welbeck	U.K. L'stone	"	2	"	0·8
∇	"	"	"	2	"	1·8
+	"	"	3175	2	1560	2·8
□	Pittsburgh	18	"	2	"	2·7

36in, 27in and 6in combustors

Fig.7.8. Empirical relation between SO_2 reduction and fluidising velocity

7.1.5 Effect of Fluidising Velocity

Increase in fluidising velocity is accompanied by the following effects:

(a) Reduction of gas residence time in the bed.

(b) Higher voidage of the bed, with reduction in the weight of solids present in a bed of given height and hence reduction of solids residence time.

(c) Bypassing of a greater proportion of the gas in bubbles.

(d) Increased throughput of coal, and hence of additive for a given Ca/S ratio and given proportion of excess air; this results in a further reduction in solids residence time.

These effects can be expected to result in poorer sulphur retention when the fluidising velocity is increased. Table 7.4 summarises the results of tests showing effects of fluidising velocity. Most of the results show that, as expected, the percentage reduction in SO_2 emission falls with increase in fluidising velocity. The results can be approximately correlated by:

$$A = X_1/V$$

where A is the Absorption Ratio, defined as the ratio of SO_2 absorbed to SO_2 emitted, i.e. (% Reduction)/(100 - % Reduction) and V is the velocity; the value of the constant X_1 depends on the operating conditions. The validity of this simple relationship can be judged from Fig. 7.8.

It is estimated that to reduce sulphur emission to 300 ppm for a 3% sulphur coal at a bed temperature of 1500°F, it would be necessary to supply about twice the quantity of additive at 8 ft/s as at 2 ft/s.

TABLE 7.4

Effect of Fluidising Velocity on % Reduction in SO_2 Emission

Coal Type	Additive Type	Sizes µm		Task	Nominal Bed Ht. ft.	Temp ^oF	Recycle	Ca/S Mol Ratio	% Reduction in SO_2 Emission at Nominal Velocity (ft/s) of:					
		Coal	Additive						2	3	4	6.5	8	11
Pittsburgh	Limestone 18	-3175	-3175	I	2	1560	No	1.7	-	-	54	-	30$^{(1)}$	-
		-3175	-3175	III	2	1560	Yes	2.7	-	-	-	85	81$^{(2)}$	77
		-3175	-3175	III	2	1560	No	2.7	-	-	-	80	-	77
		-1680	-1680	I	2	1470	No	2.2	-	84	81	-	-	-
		-1680	- 125	I	2	1560	No	1.0	-	50	50	-	-	-
Welbeck	U K Limestone	-1680	-1680	V	2	1470	No	0.8	53	45	-	-	-	-
		-1680	-1680	V	2	1470	No	1.8	86	81	-	-	-	-
		-3175	-3175	I	2	1560	No	2.8	-	-	69$^{(3)}$	-	64	-

NOTES:

(1) Extrapolated from Ca/S = 1.6

(2) Interpolated from smoothed curve

(3) Extrapolated from Ca/S = 3.0

7.1.6 Effect of Bed Height

Increase in bed height increases the residence time of both gas and solids and would be expected, therefore, to improve the percentage reduction in SO_2 emission. Table 7.5 summarises the results of comparison tests showing the effect of bed height. The first of the comparisons, for Welbeck coal with U.K. limestone, showed no change in SO_2 removal when the bed height was nearly doubled, but the remaining comparisons do show improvement. With Pittsburgh coal and Dolomite 1337 at a Ca/S mol ratio of 5.0, the percentage reduction was high even at the lowest bed height, and increasing the bed height would not be expected to cause more than a small improvement. The tests with Illinois coal and Limestone 1359 show substantial improvements in SO_2 removal on changing bed height from 2 ft to 3 ft, suggesting that, as might be expected, a bigger improvement would be obtained at low rather than at high sulphur retention.

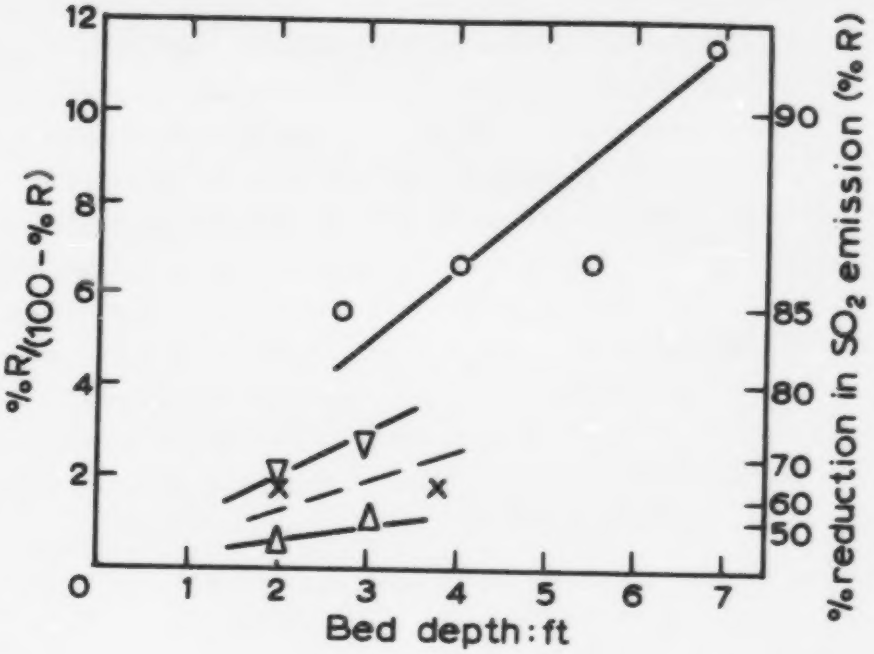
With the exception of the first comparison in Table 7.5, the results can be approximately correlated (Fig. 7.9) by the relationship:

$$A = HX_2$$

where H is bed height and A is the Absorption Ratio. The value of the constant X_2 depends on the other operating conditions.

Bed depths of about 2 ft are needed in atmospheric pressure plant to ensure good mixing of coal, and even at the highest fluidising velocities likely to be used, this depth is adequate to accommodate the heat transfer surfaces immersed in the bed. The fourfold increase in bed depth theoretically needed to compensate for an increase in fluidising velocity from 2 ft/s to 8 ft/s would cause an intolerably high pressure loss in a non-pressurised combustor. On the other hand, deep beds are needed in pressurised combustors to accommodate the required amount of heat transfer surface; fortunately high pressure drops are not a limiting factor at high pressure. The bed depth needed is broadly proportional to the pressure; it is also proportional to the fluidising velocity, and might largely compensate for the adverse effect on SO_2 reduction of increase in velocity.

In the present pilot-scale tests, and in any commercial application of fluid-bed combustion, upwards of 80% of the gas passes through the bed as bubbles. According to well-established theory there is a continual exchange between the gas in the bubbles and that in the rest of the bed which results in the high gas/solid contacting efficiency of fluidised beds. As the bubbles progress upwards through



Symbol	Coal	Additive	Size μm	Velocity ft/s	Bed temp. °F	Ca/S mol ratio
×	Welbeck	U.K.L'stone	3175	8	1560	2·8
o	Pittsburgh	1337	"	"	"	5·0
Δ	Illinois	1359	1680	3	1470	1·1
∇	"	"	"	"	"	2·2

36in and 6in combustors

Fig.7.9. Empirical relation between SO_2 reduction and bed depth

TABLE 7.5

Effect of Bed Height on % Reduction in SO_2 Emission

Coal Type and size, μm	Additive Type	Task	Nominal Vel ft/s	Temp °F	Recycle	Ca/S Mol Ratio	% Reduction in SO_2 Emission with Nominal Bed Ht (ft) of:						
							2.0	2.7	3.0	3.8	4.0	5.5	6.9
Welbeck -3175	U.K. Limestone -3175	I	8	1560	No	2.8	64	-	-	64	-	-	-
Pittsburgh -3175	Dolomite 1337 -3175	I	8	1560	No	5.0	-	$85^{(1)}$	-	-	$87^{(2)}$	87	$92^{(3)}$
Illinois -1680	Limestone 1359 -1680	V	3	1470	No	1.1	$37^{(4)}$	-	52	-	-	-	-
						2.2	64	-	$73^{(5)}$	-	-	-	-

Superscripted data extrapolated from the following Ca/S Ratios.

(1) Ca/S = 5.4
(2) Ca/S = 5.3
(3) Ca/S = 5.2
(4) Ca/S = 1.5
(5) Ca/S = 2.1

the bed they coalesce and form fewer, but larger, bubbles moving with ever-increasing velocity. In the absence of any correcting influence this results in decreasing contact efficiency with increasing bed depth. The presence of tubes in the bed is known to help in breaking up these large bubbles and restore the high gas/solid contacting efficiency. The effect of increasing bed height can therefore be expected to depend, amongst other factors, upon the amount of heat transfer surface and its distribution in the bed. Because of this, increase in bed height may be expected to be more effective in pressurised combustors in which the bed is fully packed with tubes.

7.1.7 The Effect of Operating Pressure

Increase in operating pressure whilst maintaining fluidising velocity and excess air at the same levels reduces the solids residence time in the bed in proportion to the increase in pressure (unless of course the depth of the bed is increased in proportion). From this point of view lower sulphur retention might be expected under pressure than at atmospheric pressure.

Increase in pressure can also be expected to inhibit calcination and hence pore formation. It will be seen from Fig. 7.10 that at atmospheric pressure the partial pressure of CO_2 in a boiler is below the equilibrium value at temperatures above about 1380°F, and calcination can therefore occur in this region. At operating pressure greater than 2 atm, the partial pressure of CO_2 in a boiler is above equilibrium at 1470°F, and since calcination is therefore impossible, poor performance would be expected in a pressurised combustor with limestone. The equilibrium partial pressure for calcination of $MgCO_3$ at all combustor temperatures is very high, so that the $MgCO_3$ in dolomite can be expected to calcine in pressurised combustors giving access to internal surfaces and satisfactory sulphur retention.

The results of the tests in the pressurised combustor are detailed in Table 4.9 and shown in Fig. 4.9 of Section 4. Dolomite was markedly more effective than limestone on the basis of the Ca/S mol ratio. The quantity of additive required to achieve a required level of emission is also less with dolomite than with limestone on a weight basis. For example, to achieve 300 ppm when burning a 3% sulphur coal would require about 7.6 lb/lb sulphur for dolomite as compared with an estimated 10 lb/lb sulphur for limestone. This result was to be expected from theoretical considerations and from the results of the porosity measurements from calcination experiments in the laboratory (Appendix 8). The performance with the limestone additive was, however, not as poor as had been expected. This may be due partly to chemical and physical characteristics of the particular additive (Limestone 18) used in the tests, and partly to attrition in the combustor of the $CaSO_4$ layer on the surface of the particles.

Comparison of the performance of the pressurised and non-pressurised combustors (Table 7.6) when using dolomite as the additive shows that sulphur retention efficiency for the pressurised combustor is well above that for the non-pressurised without recycle of carryover, but is below the performance attained with positive recycle.

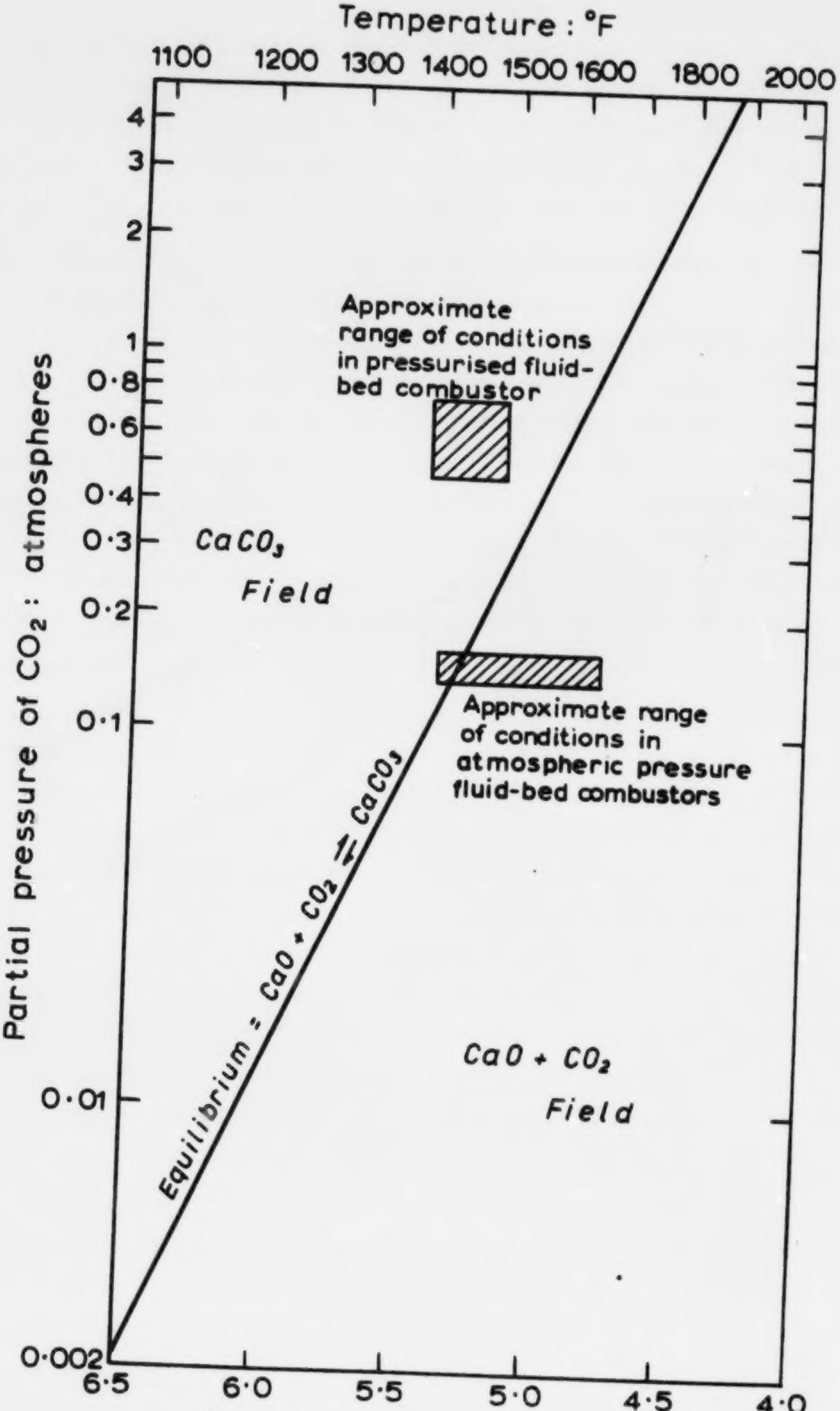


Fig. 7.10. Equilibrium diagram for the $CaCO_3/CO_2$ system in relation to conditions in fluidised bed combustors

It is considered that the slightly poorer performance of the pressurised combustor compared with the non-pressurised combustor with recycle reflects the inferior efficiency of the recycle system on the pressure combustor and that any effect of pressure is small.

Table 7.6 Comparisons of % Reduction in SO_2 Emission at Atmospheric and at High Pressure

Coal: Pittsburgh Temperature: 1470°F

Pressure Atm Abs.	Additive		Task	Bed Ht. ft.	Velocity ft/s	Ca/S Mol Ratio	Recycle	% Reduction in SO_2 Emission
	Type	Size µm						
1	Dolomite 1337	-1680	I	3.7	2.1	2.0	No	80(1)
3.5		-1587	II	3.8	1.9	2.0	Yes(2)	97(3)
5		-1587	II	3.8	2.0	2.0	Yes(2)	98
1	Dolomite 1337	-1680	I	3.8	2.2	1.6	Yes(4)	99
5		-1587	II	3.8	2.0	1.6	Yes(2)	94(5)
1	Limestone 18	-1680	I, V	2.0	3.0	1.9	No	77(6)
5		-1587	II	3.8	2.0	1.9	Yes(2)	66
1	Limestone 18	-1680	I, V	2.0	3.0	2.4	No	87(6)
5		-1587	II	3.8	2.0	2.4	Yes(2)	77

NOTES:

(1) Extrapolated from Ca/S = 2.2

(2) Recycle system thought to be ineffective

(3) Extrapolated from Ca/S = 1.9

(4) Positive recycle of fines

(5) Interpolated from Fig. 4.11

(6) Interpolated from Fig. 7.1

7.1.8 The Effect of Recycle

Fines elutriated from fluidised combustors contain unconsumed carbon, and the loss of carbon can be reduced by recycling the fines. Since the elutriated fines contain incompletely utilised additive it can be expected that fines recycling will also improve the percentage reduction in SO_2 emission. Table 7.7 summarises the data on the effect of recycling. It should be emphasised that the only positive recycle systems were those employed in the 36 in and 27 in combustors; the 24 in x 48 in pressure combustor, and 12 in and 6 in non-pressurised combustors had cyclones with internal dip-leg, and were probably less effective than the efficiences for which they were designed.

Table 7.7 Effect of Fines Recycle on % Reduction in SO_2 Emission

Coal Type and size, µm	Additive Type and size, µm	Task	Nom Bed Ht.ft.	Nom Vel ft/s	Temp °F	Ca/S Mol Ratio	% Reduction	
							Without Recycle	With Recycle
Pittsburgh -3175	Limestone 18 -3175	III	2	8	1550	1.9	56*	62(1)
		III	2	6.5	1540	2.7	80(2)*	85
		III	2	10.9	1560	2.7	78(3)*	77
Pittsburgh -3175	Limestone 18 - 150	III	2	8	1550	1.9	50(1)*	33
Pittsburgh -1680	Dolomite 1337 -1680	I	3.8	2	1470	1.6	73(4)	99
Welbeck -1680	UK Limestone -1680	V	2	2	1470	0.8	53	55
		V	2	3	1470	0.8	45	75

* With internal recycle only

NOTES:
(1) Extrapolated from Ca/S = 1.6
(2) Extrapolated from Ca/S = 2.8
(3) Extrapolated from Ca/S = 2.6
(4) Extrapolated from Ca/S = 2.2

The comparison for Pittsburgh coal with Dolomite 1337 obtained from the 36 in combustor shows that a substantial improvement was obtained. One of the two comparisons for Welbeck coal with U.K. Limestone from the 6 in combustor shows a marked improvement, but the other does not.

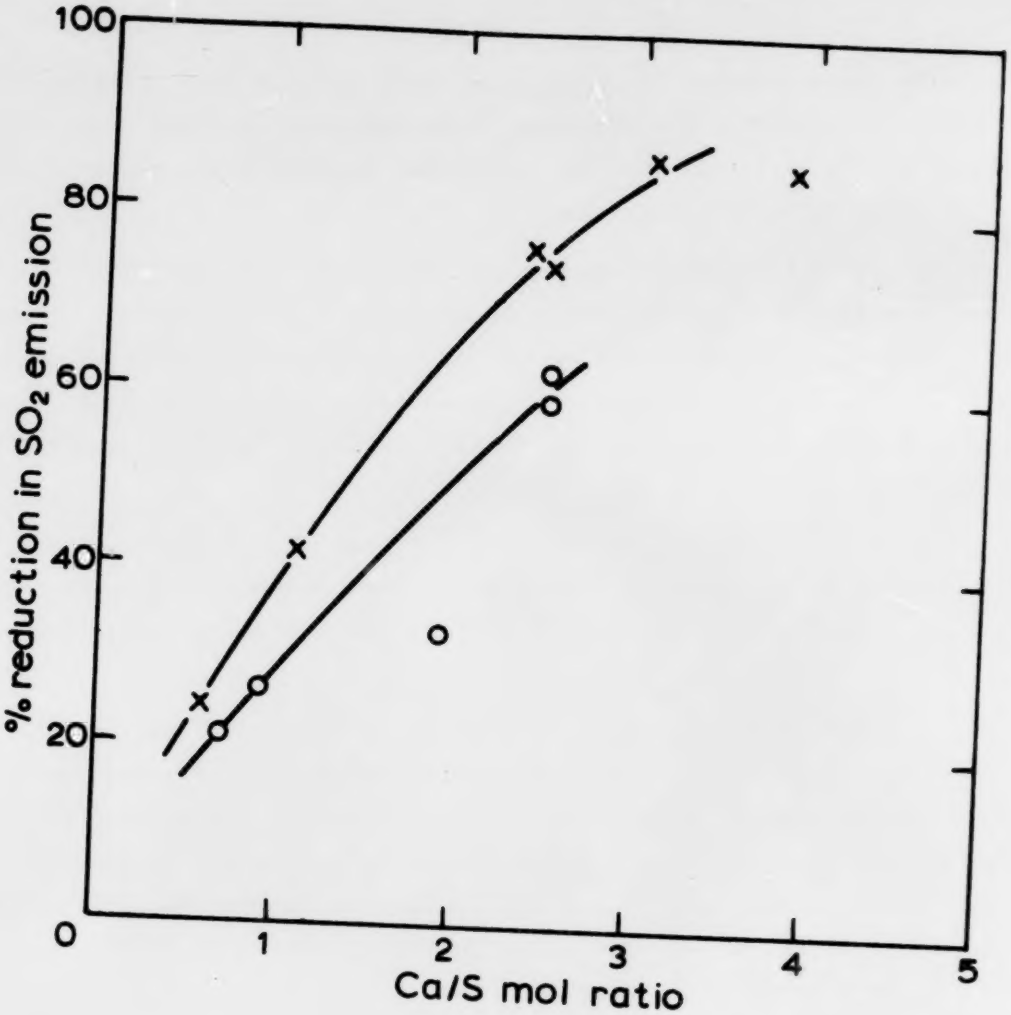
The remaining comparisons were obtained from tests in the 27 in rig which had a medium efficiency internal cyclone, in operation at all times. It is possible, however, that the hopper system did not operate sufficiently quickly to cope with the greater dust loading when the external cyclone was in operation. This may account for the anomalous effect of recycle in the third and fourth comparisons in Table 7.7.

It is concluded that recycle of fines (particularly where the cyclone has a low cut size) is beneficial and that in those circumstances where this was not clearly shown, the effectiveness of the recycle system is open to doubt.

It may not, however, be feasible to exploit fines recycle fully in commercial plant. Recycling fines involves engineering problems and, except in a few special circumstances where highly efficient internal cyclones can be envisaged, the recycled material causes a thermal load on the fluid-bed. These problems are clearly greater at high fluidising velocities and it is likely that less efficient re-circulation cyclones would then be used to limit the amount of material in circulation. It should also be noted that, as discussed in Section 7.5 fines recycle increases particulate emission.

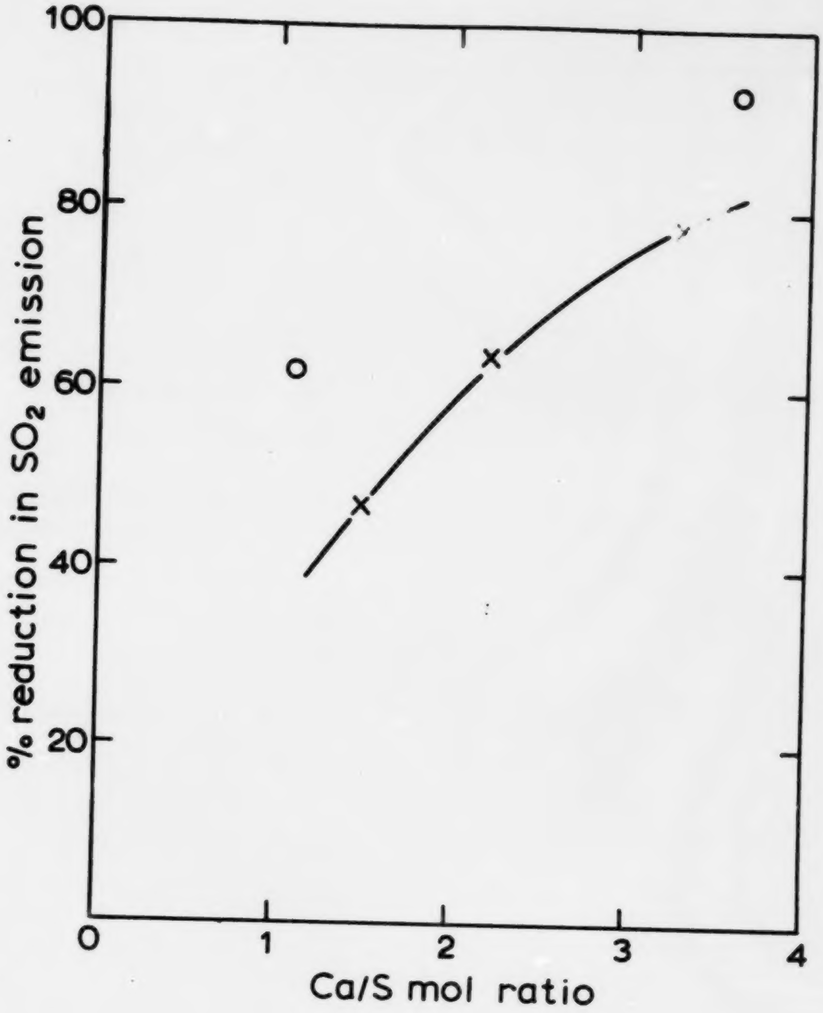
7.1.9 Effect of Additive Particle Size

The rates of many gas-solids reactions are proportional to the solid surface area, and are therefore an inverse function of particle size. In fluidised combustion systems, therefore, reduction in additive particle size should improve SO_2 removal, particularly for additives where the internal surface becomes obscured by an impervious shell of calcium sulphate. However, reduction in particle size may result in rapid elutriation of the additive and hence reduce the residence time in the bed from as much as several hours to as little as a few seconds, and the net effect may be a reduction in SO_2 removal efficiency. Further reduction in particle size below that at which rapid elutriation occurs will not greatly affect the residence time of particles in the bed, and hence would be expected to improve SO_2 retention. Therefore there may be an optimum particle size for coarsely crushed additive, below which retention decreases to a minimum and then increases for very fine particles. With both coarse and fine additive, the SO_2 removal efficiency would, in general, be expected to fall with increase in velocity



Pittsburgh coal
Limestone 18
Bed depth: 2ft
Fluidising velocity: 8ft/s
Bed temperature: 1550°F
With recycle
27in combustor
Particle size {x -3175 µm
o -150 µm

Fig. 7.11. Effect of additive particle size on SO_2 reduction (high fluidising velocity)



Illinois coal
Limestone 1359
Bed depth: 2ft
Fluidising velocity: 3ft/s
Bed temperature: 1470°F
No recycle
6in combustor

Particle size $\begin{cases} \times -1680\,\mu m \\ \circ -125\,\mu m \end{cases}$

Fig. 7.12. Effect of additive particle size on SO_2 reduction (low fluidising velocity)

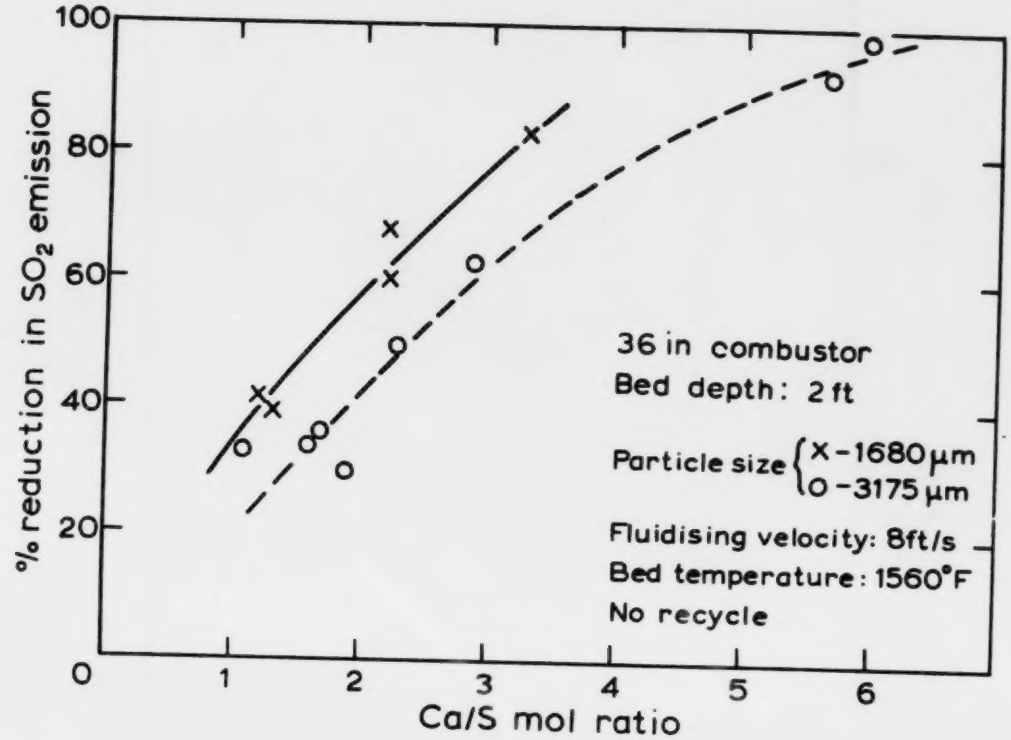


Fig. 7.13. Effect of additive particle size on SO_2 reduction (Limestone 18)

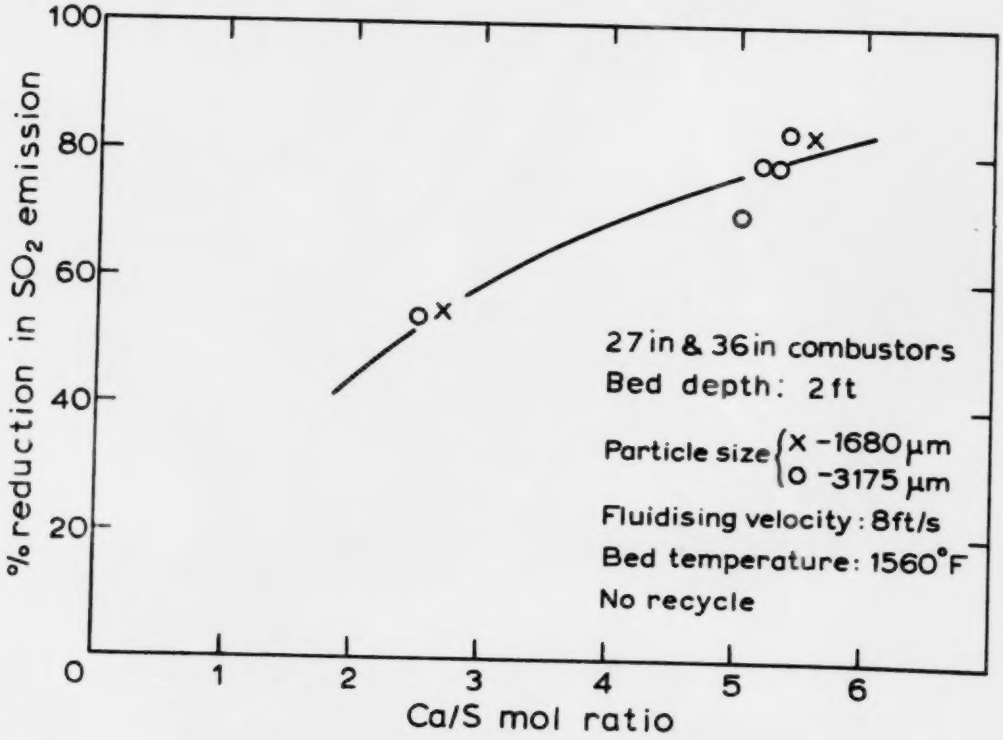


Fig. 7. 14. Effect of additive particle size on SO_2 reduction (Dolomite 1337)

The results of tests which had the main objective of determining the effect of particle size are shown in Table 7.8 and in Figs. 7.11 and 7.12. Additional data obtained over a range of fluidising velocities and bed height have been extrapolated to common operating conditions using the correlations in Sections 7.1.5 and 7.1.6 and are given in Figs. 7.13 and 7.14.

Table 7.8 Effect of Additive Particle Size on % Reduction in SO_2 Emission

Coal Type	Additive Type	Task	Nom Bed Ht. ft.	Nom Vel ft/s	Temp °F	Recycle	Ca/S Mol Ratio	% Reduction for Additive Size(μm) of			
								-3175	-1680	- 150	- 125
Pittsburgh	Limestone 18	I	2	4	1560	No	1.7	54	68(1)	-	69(2)
		III	2	6.4	1550	Yes	2.8	86(3)	-	83	-
		III	2	8	1550	Yes	1.0	38(4)	-	28(4)	-
		III	2	8	1550	Yes	2.0	65(4)	-	50(4)	-
Illinois	Limestone 18	V	2	3	1470	No	1.1	-	39(5)	-	62
		V	2	3	1470	No	3.6	-	81(5)	-	93

NOTES:
(1) Extrapolated from Ca/S = 1.3
(2) Extrapolated from Ca/S = 1.0
(3) Temperature = 1525°F
(4) Interpolated from Fig. 7.11
(5) Interpolated from Fig. 7.12

Fig. 7.13 indicates that a reduction in the limestone particle size from -3175 μm to -1680 μm improved SO_2 reduction; this reduction in size would not be expected to affect elutriation significantly. Fig. 7.14 indicates that a similar size reduction for dolomite has no effect, suggesting that access to internal surface is not a limiting factor for dolomite.

Reduction of additive particle size to less than about 150 µm results in poorer sulphur retention at high velocities (Fig. 7.11) but improves retention at low velocities (Fig. 7.12).

The former is in contrast to the results published by Pope, Evans and Robbins[5]; they show that for Limestone 1359 at a Ca/S mol ratio of 2.6, with velocities of 12 ft/s in a bed only 10 inch deep, 80% retention was obtained when the limestone was ground to -44 µm, and 60% retention with -74 µm limestone. This is in line with the initial comments, namely, that decrease in size down to a certain level will result in a reduction in SO_2 retention, but that further decrease in size is likely to result in an improvement in SO_2 retention.

7.1.10 Effect of type and source of additive

It was shown in Section 6.2 that the structure (porosity) of the calcined/sulphated limestone particles varies with the source of the stone, and that dolomites behave in a different manner from limestone.

In the pilot-scale programme three limestones and two dolomites were used. Data comparing Limestone 18 with U.K. Limestone are shown in Fig. 7.15 and Limestone 1359 with U.K. Limestone in Fig. 7.16. From these figures it can be deduced that Limestone 18 is more effective than U.K. Limestone which in turn is more effective than Limestone 1359.

Further data for operation at atmospheric pressure are tabulated in Table 7.9. These show that Limestone 18 is more effective than Dolomite 1337 except at low temperatures (1380°F). Comparison of the data at 1470°F in Table 7.9 with Fig. 7.15 suggest that Dolomite 1337 is similar to U.K. Limestone.

Thus on a molar basis the above four additives can be placed in descending order of effectiveness as follows:

Limestone 18
U.K. Limestone and Dolomite 1337
Limestone 1359

This order of effectiveness may be compared with that indicated by the laboratory sulphation test, Fig. 6.1. In this test, the Dolomite 1337 was slightly superior to Limestone 18 and both were markedly better than Limestone 1359. The difference between the behaviour in the fluidised bed and in the laboratory is thought to be due to attrition of the particle surface in the fluidised bed. In the laboratory test (Section 6.2.2) it was found that access of SO_2 to the interior of limestone particles was reduced with increasing degree of sulphation.

TABLE 7.9

Effect of Type of Additive on % Reduction in SO_2 Emission

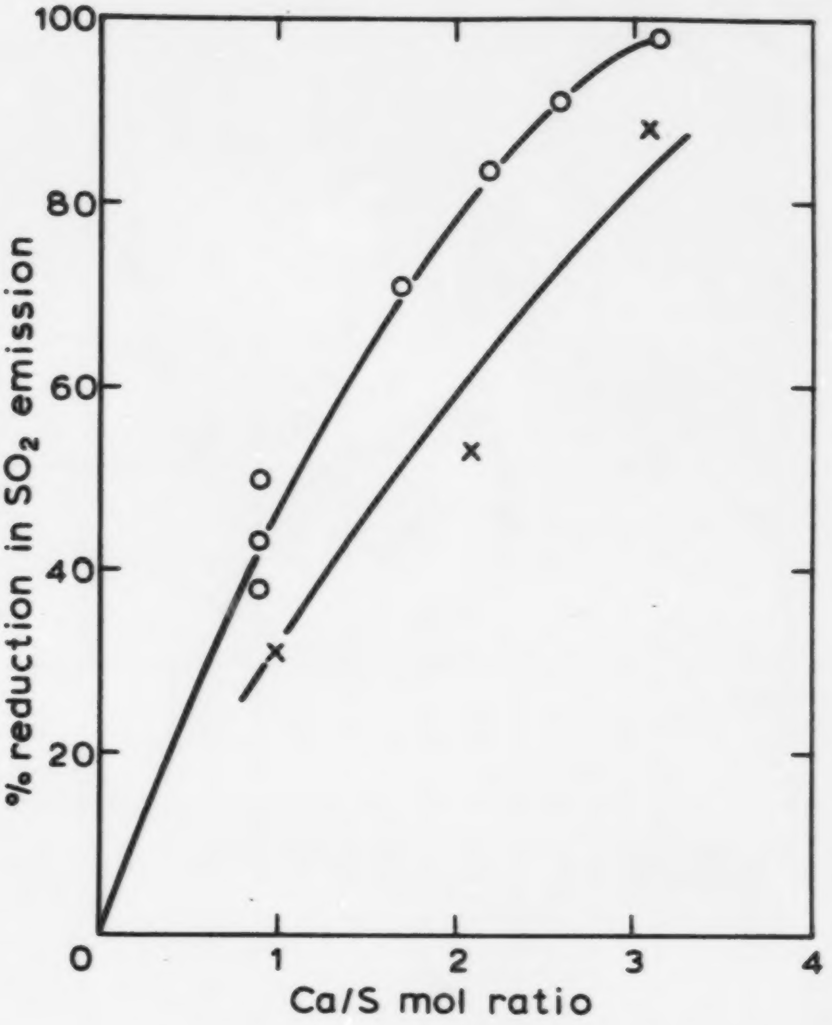
Coal Type and Size, µm	Additive Type and Size, µm	Task	Nominal bed Ht. ft.	Temp °F	Recycle	Fluidising velocity ft/s	Ca/S mol ratio	% Reduction in SO_2 emission
Pittsburgh -1680	Limestone 18 -1680	I	2	1380	No	4	2.2	50
	Dolomite 1337 -1680	I	2	1380	No	4	2.2(1)	66
	Limestone 18 -1680	I	2	1470	No	4	2.2	81
	Dolomite 1337 -1680	I	2	1470	No	4	2.2(2)	67
	Limestone 18 -1680	I	2	1560	No	4	2.2	82
	Dolomite 1337 -1680	I	2	1560	No	4	2.2(2)	53
Pittsburgh -3175	Limestone 18 -3175	I	3.8	1560	No	8	5.7	96
	Dolomite 1337 -3175	I	3.8	1560	No	8	5.7(3)	90
Welbeck -3175	Limestone 18 -1680	V	2	1470	No	3	1.9	78
	U.K. Limestone -1680	V	2	1470	No	3	1.9(4)	83

(1) Extrapolated from Ca/S = 2.6

(2) Extrapolated from Ca/S = 2.7

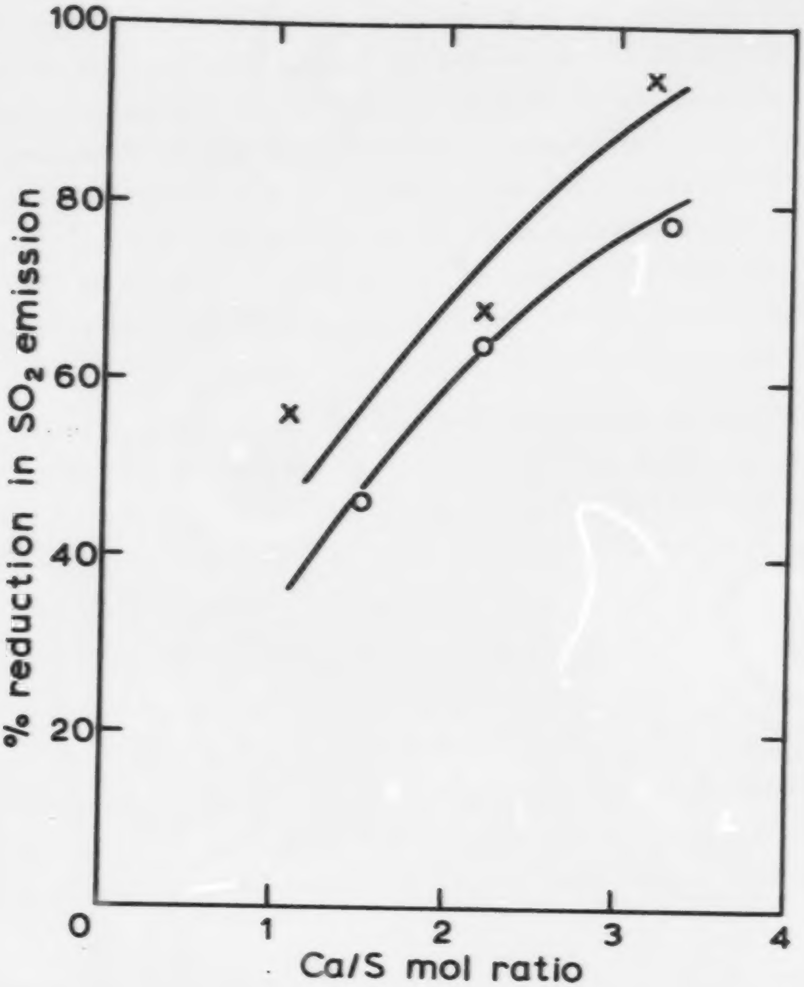
(3) Extrapolated from Ca/S = 5.3

(4) Extrapolated from Ca/S = 1.8



Pittsburgh coal (−1680 μm)
Bed depth: 2ft
Fluidising velocity: 3ft/s
Bed temperature: 1470°F
No recycle
36in and 6in combustors
○ Limestone 18
× U.K. Limestone

Fig.7.15. Comparison of SO_2 reduction with Limestone 18 and U.K. Limestone



Illinois coal (−1680 μm)
Bed depth: 2ft
Fluidising velocity: 3ft/s
Bed temperature: 1470°F
No recycle
6in combustor
o Limestone 1359
x U.K. Limestone

Fig.7.16. Comparison of SO_2 reduction with Limestone 1359 and U.K. Limestone

In Limestone 18 this was due to progressive reduction of the large 'transport pores'; in Limestone 1359 there was an absence of 'transport pores' and an impermeable surface layer of sulphate was rapidly formed. Attrition of the particle surface would thus account for the small improvement in sulphur retention for Limestone 18 and the large improvement for Limestone 1359, both relative to the performance of Dolomite for which access to the internal surface is not a limiting factor. The absence of a sulphated surface layer on Limestone 1359 particles from one of the fluidised bed combustors (see Section 6.2.3.) provides direct evidence that attrition of the surface layer was occurring in the bed.

It should be remembered that the calcium content of dolomites is considerably lower than that of limestones (see Table 3.2, Section 3), and that Limestone 18 has a somewhat lower calcium content than other limestones. Thus on a weight basis, the above order of effectiveness is changed to:

Limestone 18
U.K. Limestone
Limestone 1359
Dolomite 1337

With Limestone 18 only slightly superior to U.K. Limestone. An anomalous result, indicating a slight superiority of U.K. Limestone over Limestone 18, was obtained with Welbeck coal. This anomaly might be due to the low sulphur content of the coal.

It was shown in Section 7.1.7 that under pressure Dolomite 1337 is markedly superior to Limestone 18 on both molar and weight bases, but the retention by the uncalcined Limestone 18 was better than expected, again probably because of attrition of the surface layer of sulphate. U.K. Dolomite used with Welbeck coal gave better percentage SO_2 reduction than Dolomite 1337 with Pittsburgh coal, but this might again be an effect due to the coal rather than the dolomite.

Efficient utilisation of additive is important from the point of view of minimising thermal losses. In addition to sensible heat losses, calcination is endothermic:

$$CaCO_3 = CaO + CO_2 - 43 \text{ kcal/gmol} \quad (298^\circ K)$$

$$MgCO_3 = MgO + CO_2 - 24 \text{ kcal/gmol} \quad (298^\circ K)$$

However, sulphation is strongly exothermic:

$$CaO + SO_2 + \tfrac{1}{2}O_2 = CaSO_4 + 120 \text{ kcal/gmol} \quad (298^\circ K)$$

With a high utilisation of stone, e.g. 85% reduction of SO_2 emission from a 3% sulphur coal with a Ca/S mol ratio up to about 2, there is approximately a thermal balance for limestone at atmospheric pressure, and a heat loss with dolomite of up to about 1½% of the thermal input to the boiler. At a Ca/S mol ratio of 4 the heat losses incurred to achieve 85% SO_2 reduction are increased to 2% for limestone and 4% for dolomite. Under pressure, calcination of $CaCO_3$ is inhibited, and the heat losses are consequently reduced. For example, the heat loss for 85% SO_2 reduction with dolomite under pressure would be negligible at Ca/S mol ratios up to 2, and only 2% of the coal heat input at a Ca/S mol ratio of 4.

7.1.11 Effect of coal type

The most important coal property is obviously the sulphur content, since the actual feed rate of additive required for a given percentage SO_2 reduction is approximately proportional to this. Also, the percentage SO_2 reduction which must be achieved in order to obtain a particular SO_2 emission is lower with a low-sulphur coal. Secondary considerations are the amount of calcium present in the ash, which affects the emission of SO_2 without additive, and the total amount of ash, which affects the residence time of solids in the bed. In order to allow direct comparison of the effect of the operating variables with the various coals, the effect of sulphur and calcium content has been eliminated by plotting the results as the percentage SO_2 reduction against the molar ratio of added calcium to total sulphur in the coal, Fig. 7.17. This approach is based on the assumptions that the process of SO_2 reduction is directly proportional to the SO_2 concentration in the gas, and the close agreement between the results from the four coals plotted on this basis confirm that this is a good approximation. However, at any given Ca/S mol ratio the percentage SO_2 reduction for Welbeck coal was higher than for the other three coals; there may also be some smaller differences between the other coals.

The better reduction with Welbeck coal could not be explained in terms of the coal rank, as measured by the volatile matter or caking capacity of the coal. It was found that the rate of release of pyritic sulphur from coal is about an order of magnitude more rapid than that of organic sulphur, with the actual rates differing between coals. The total rate of sulphur release from Welbeck coal was more rapid than for Pittsburgh (the other coals were not tested), and this may have led to a lower proportion of the sulphur release in the combustor being from elutriated fines in the freeboard, where reaction with stone is inefficient.

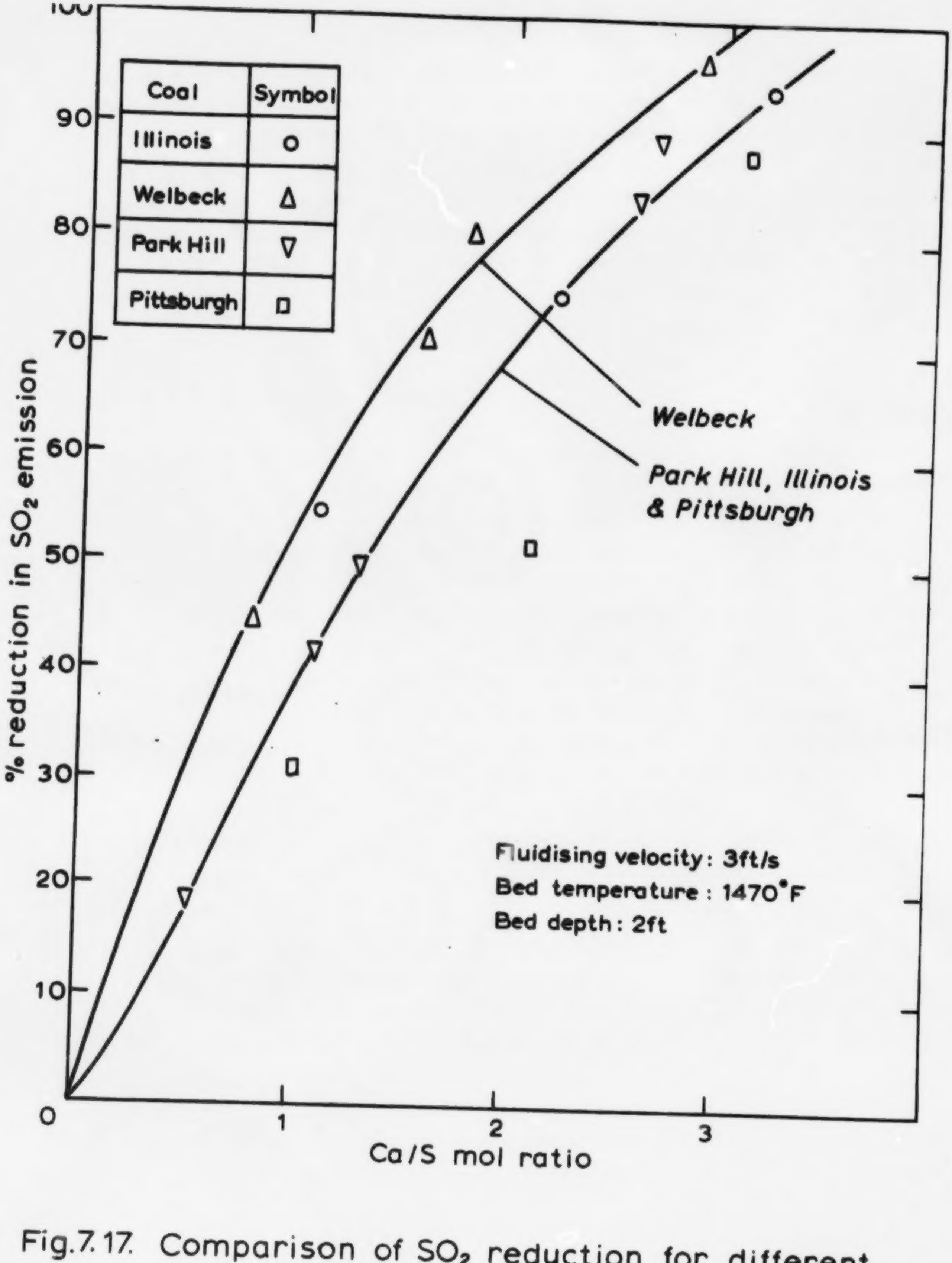


Fig.7.17. Comparison of SO_2 reduction for different coals with U.K. Limestone

An alternative explanation is that because of the low feed rate of additive with the low-sulphur Welbeck coal, the residence time of coarse additive particles in the bed is longer. This may be expected to allow a higher utilisation of the stone, particularly if the process of attrition is involved, and hence, since the Ca/S mol ratio is the same, a higher reduction of SO_2 emission is obtained.

7.1.12 The approach to steady state

In the context of this discussion, the approach to steady state is the attainment of a new level of SO_2 emission after making a change in operating conditions. The time to reach steady state is not always the same as that required for the concentration and sulphation of additive particles in the bed to reach their final values.

Changes in bed composition often occur slowly. For example, starting with an additive-free bed in the pressure combustor, a steady SO_2 emission was established after about 60 hours when dolomite was fed at a Ca/S mol ratio of about 0.8 (Appendix II, Fig. A2.3.1). Comparison of the analyses of the bed material at this time with those during the subsequent 40 hours operation showed that some bed composition changes were still occurring. On the other hand, the final SO_2 emission level was reached after only 25 hours in a test started with a partly sulphated bed (Fig. 7.18). Although the approach to steady state was slow in both instances, the response of SO_2 readings to fluctuations in coal feed rate (and possibly the Ca/S ratio) was rapid.

The behaviour with limestone in the pressurised combustor was different. The SO_2 emission reached its minimum value within about six hours of starting to feed limestone. The retention efficiency was lower and the fluctuations in SO_2 emission greater in amplitude and frequency than with dolomite. It might be expected that with limestone, which is significantly more reactive when the extent of sulphation is low, steady state conditions would be achieved before the total calcium inventory had stabilised. This would explain a much more rapid approach to steady state SO_2 emission with limestone.

Experiments at atmospheric pressure in the 6 in combustor also showed the relative unimportance of achieving a stable limestone concentration. After six hours' operation, the percentage SO_2 reductions were:

(a) 43% after starting with a lime-free bed and

(b) 38% after starting with a lime-rich bed.

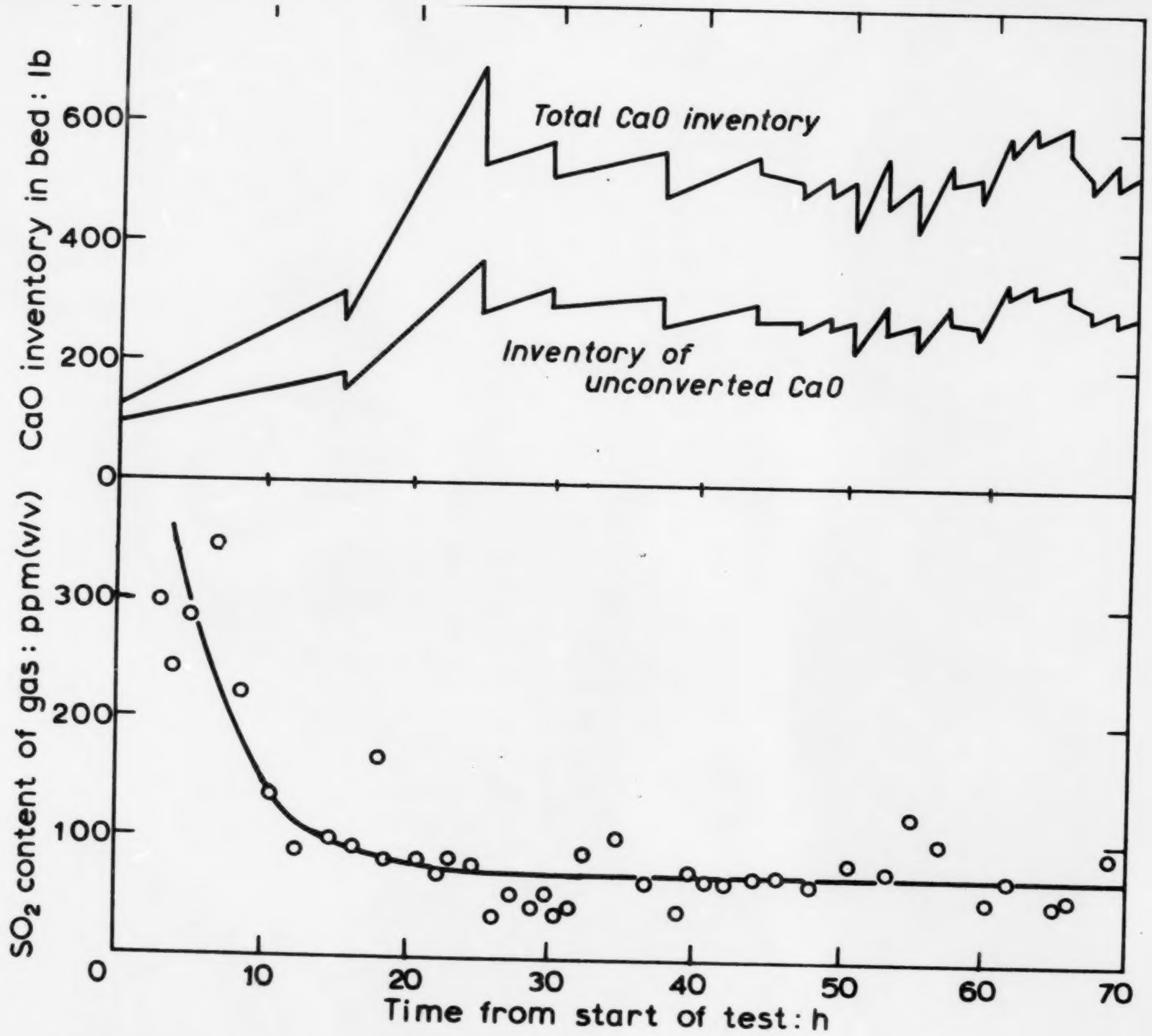


Fig. 7.18. Variation of SO_2 emission and of total and unconverted CaO inventories in 48in X 24in Combustor

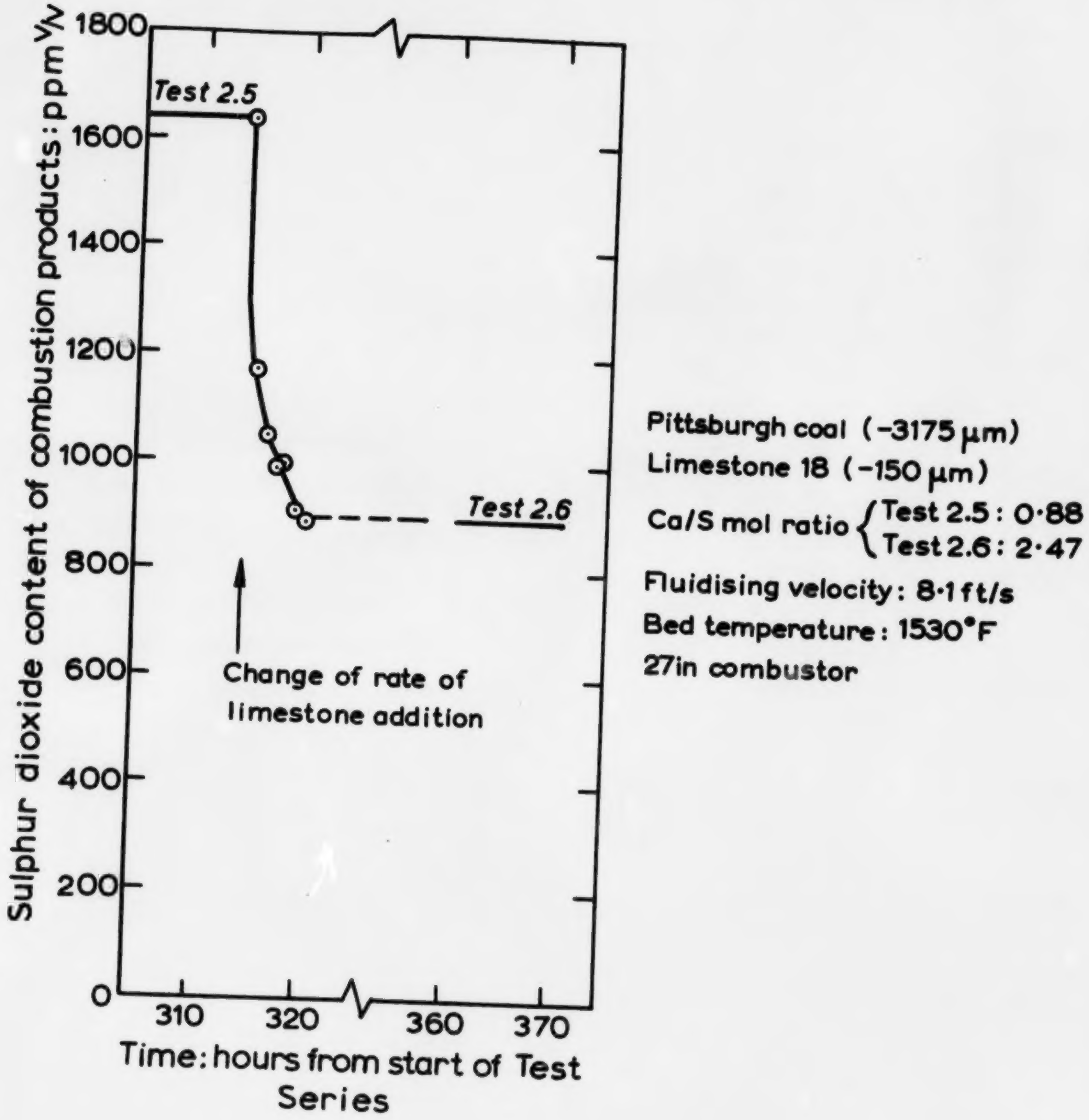


Fig.7.19. Variation of SO_2 emission after increasing rate of limestone addition in 27in Combustor

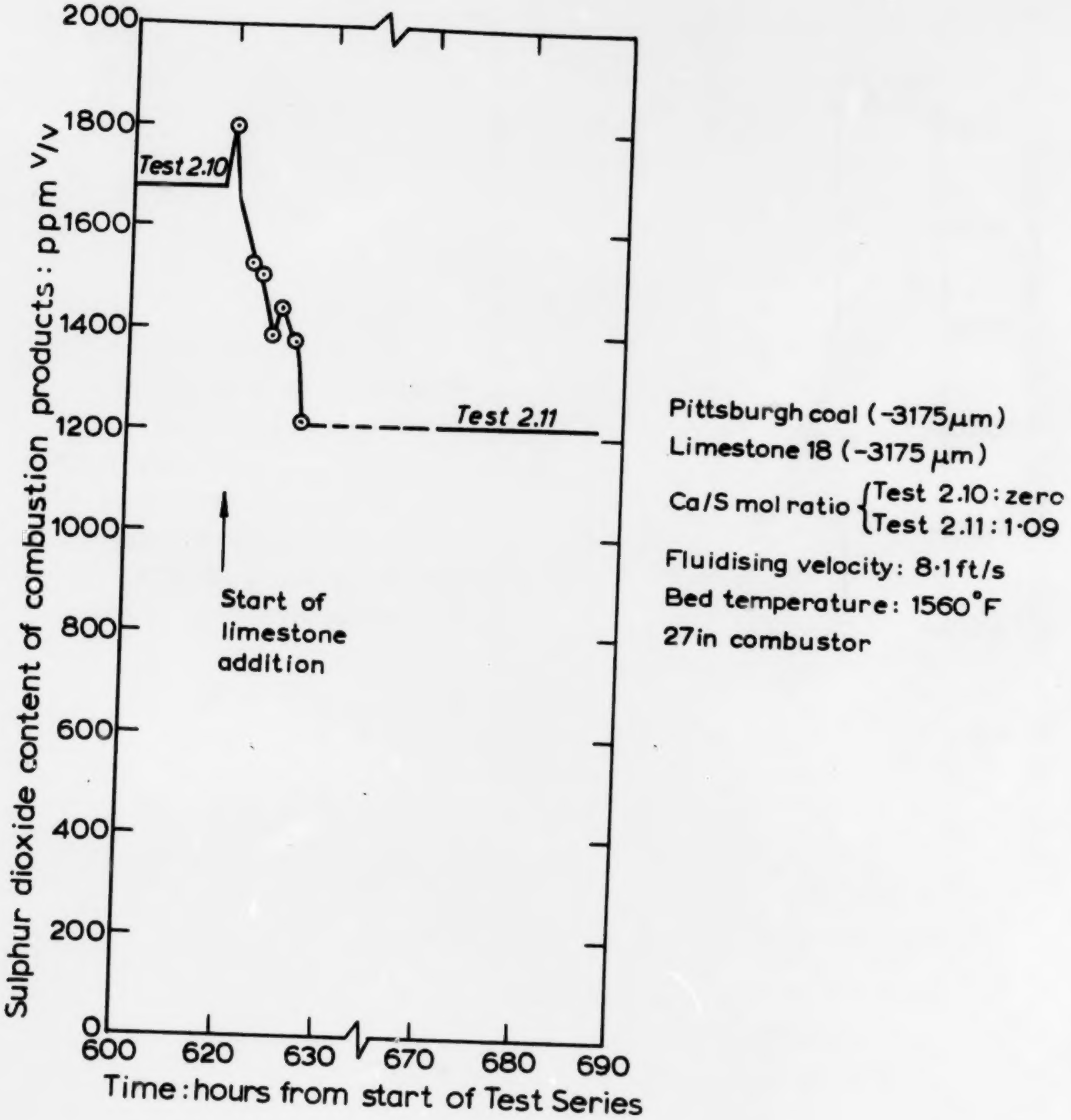


Fig.7.20. Variation of SO_2 emission after restarting limestone addition in 27in Combustor

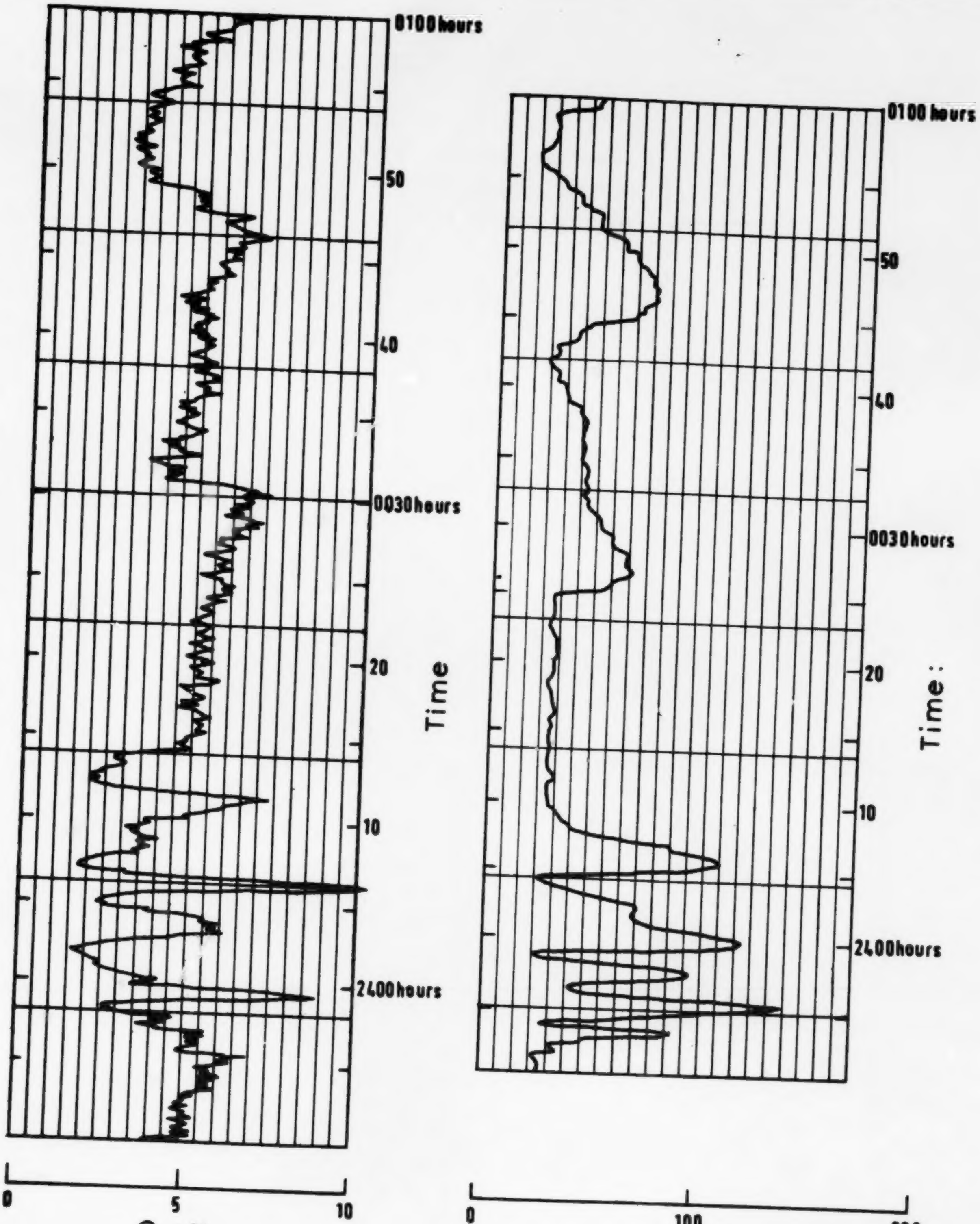


Fig. 7.21 Variation of SO_2 emission with O_2 concentration in 48in. x 24in. combustor

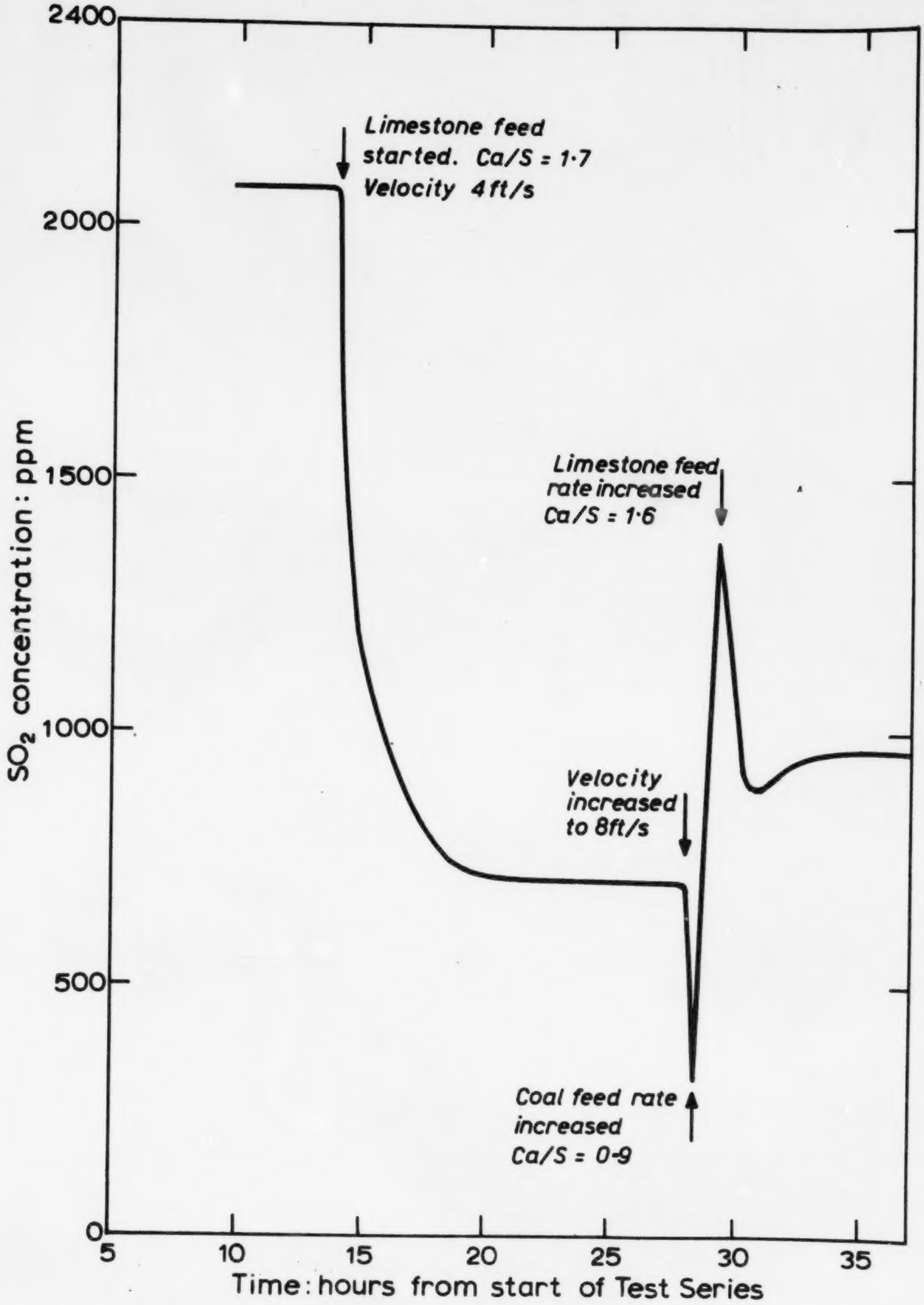


Fig. 7. 22. Variations of SO_2 emission after changes in operating conditions in 36in Combustor

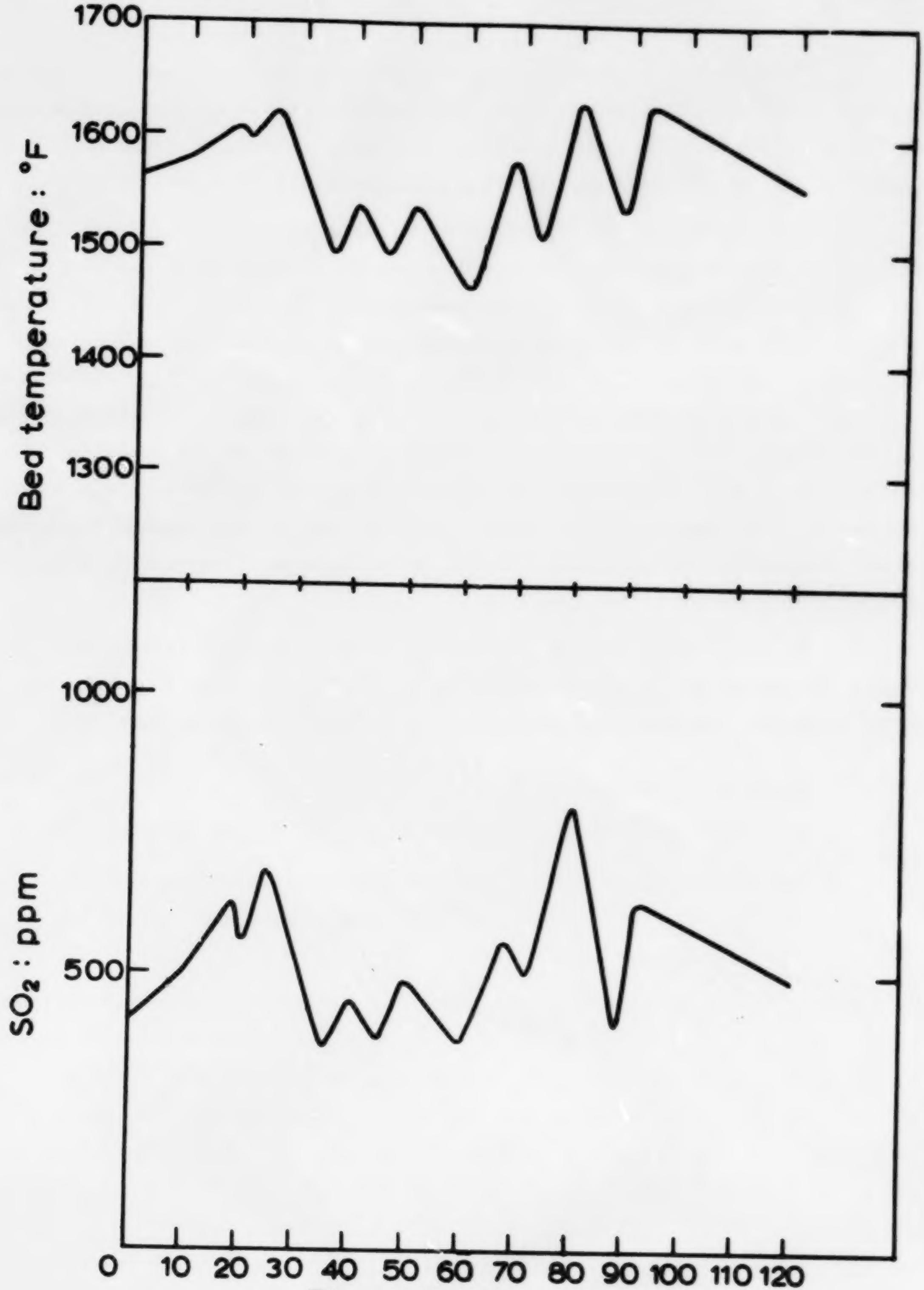


Fig.7. 23. Variation of temperature and SO$_2$ emission during a bed temperature survey in the 36in Combustor

The approach to steady state SO_2 emission during a long term test on the 27 in combustor is shown in Fig. 7.19 for operation with -150 µm limestone, and in Fig. 7.20 for -3175 µm limestone. It will be seen that the SO_2 concentration had achieved the new levels after approx. 7 hours' operation.

The sensitivity of SO_2 emission to fluctuations in coal feed rate at constant rate of air input (depicted by the O_2 concentration in the flue gases) is shown for the 48 in x 24 in combustor in Fig. 7.21. It will be seen from Fig. 7.22 that in the 36 in combustor, after doubling the throughput (increasing fluidising velocity from 4 ft/s to 8 ft/s and doubling the coal feed rate), and taking into account the attendant fluctuations in the change, steady conditions were achieved within six hours. Comparison of the behaviour shown in Fig. 7.21 with that in Fig. 7.22 suggests that, unless there is adequate time for the bed composition to change, fluctuations in the sulphur input rate are not matched by corresponding changes in the rate of retention, and result in large fluctuations in SO_2 emission.

The very rapid response of SO_2 emission to changes in temperature (Fig. 7.23) shows that the adverse effect of high temperature is reversible and is therefore not due to sintering or slag formation on the particles.

7.1.13 Accuracy of the results

The reproducibility of the data depends on errors arising from

(a) determination of the SO_2 concentration in the gas; and

(b) reproducibility of those operating conditions that affect the absorption of SO_2.

The reproducibility of determination of the SO_2 concentration, assessed from 36 tests in Tasks I, III, IV and V in which no additive was used, was found to be approx. ± 10%, which is within the generally accepted limits (Boiler Availability Committee Bulletin No. MC/316). In considering the reproducibility of operating conditions, it has been shown that variations of Ca/S mol ratio, bed temperature, fluidising velocity, bed height and additive particle size have a smaller effect when the percentage reduction in SO_2 emission is high (i.e. when the emission is low), so that it can be assumed that the reproducibility of SO_2 absorption will be better at high percentage reductions. The reproducibility of SO_2 emission during tests in which additive was used has been assessed from 21 tests (10 replicate sets) in Tasks I, II, III and V, and found to be ± 29%. Taking into account the ± 10% analytical error associated with the emission without additive, this results in a reproducibility of percentage reduction of ± 15% at 50% SO_2 reduction or ± 5% at 85% reduction when the datum SO_2 emission is 2000 ppm. Differences between single results within these limits may not be significant, but smaller differences between sets of results, e.g. between curves through sets of points, are meaningful

7.1.14 The mathematical model

Application and testing of the mathematical model against plant data has shown that good predictions are obtained for tests with coarse dolomite (pressurised combustor, Test Series 2 and 3). This is because with coarse dolomite the processes of elutriation and attrition, for which rate constants are uncertain, are not rate controlling. The agreement obtained for this case demonstrates the validity of the treatment of sulphur retention in the mathematical model. For additives of wide size distribution the predicted sulphur retention is sensitive to the values used for the elutriation rate constants of the close size fractions. For limestones, and for Limestone 1359 in particular, the predicted retention is also dependent on the value of the attrition rate constant.

Published elutriation rate data show considerable scatter, but it can be seen in Fig. 7.24 that in order to achieve good agreement with experimental results for Limestone 18 without allowing for attrition, it was necessary to use values at the extreme minimum of the range of published elutriation rates, (the rate constants decrease with increasing value of the empirical constant n). Fig. 7.25 shows that by allowing for attrition of particles in the bed the results for Limestone 1359 can be predicted when using reasonable elutriation rates (n = 1). Attrition is assumed to be described by the equation

$$\frac{dx}{dt} = - K_d \, x$$

where x is the particle size

K_d is the attrition rate constant, h^{-1}

t is the residence time in the bed, h

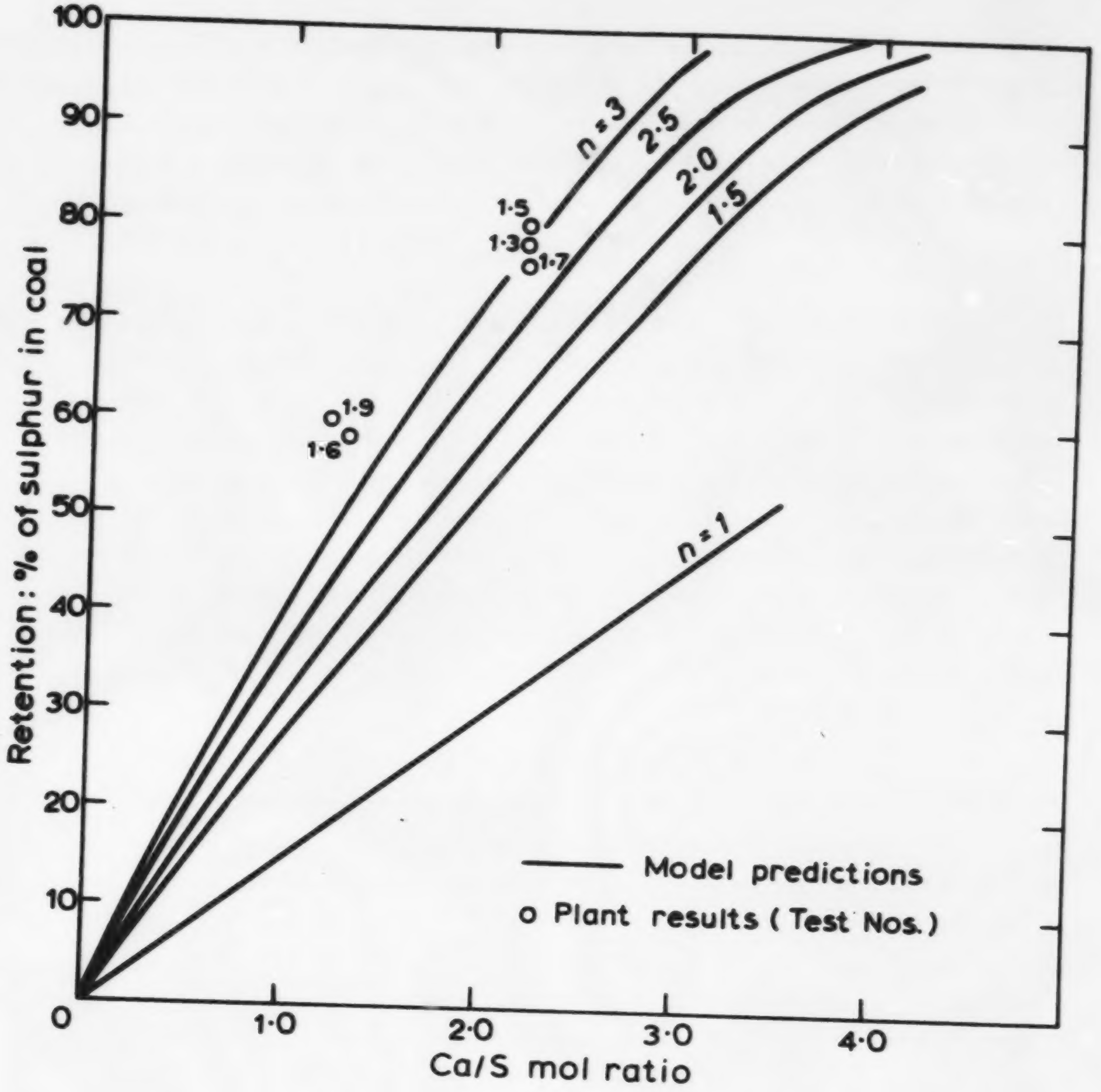


Fig. 7. 24 Comparison of predictions for Limestone 18 with experimental results of Task I, showing effect of decreasing elutriation rates (increasing value of n) with no attrition

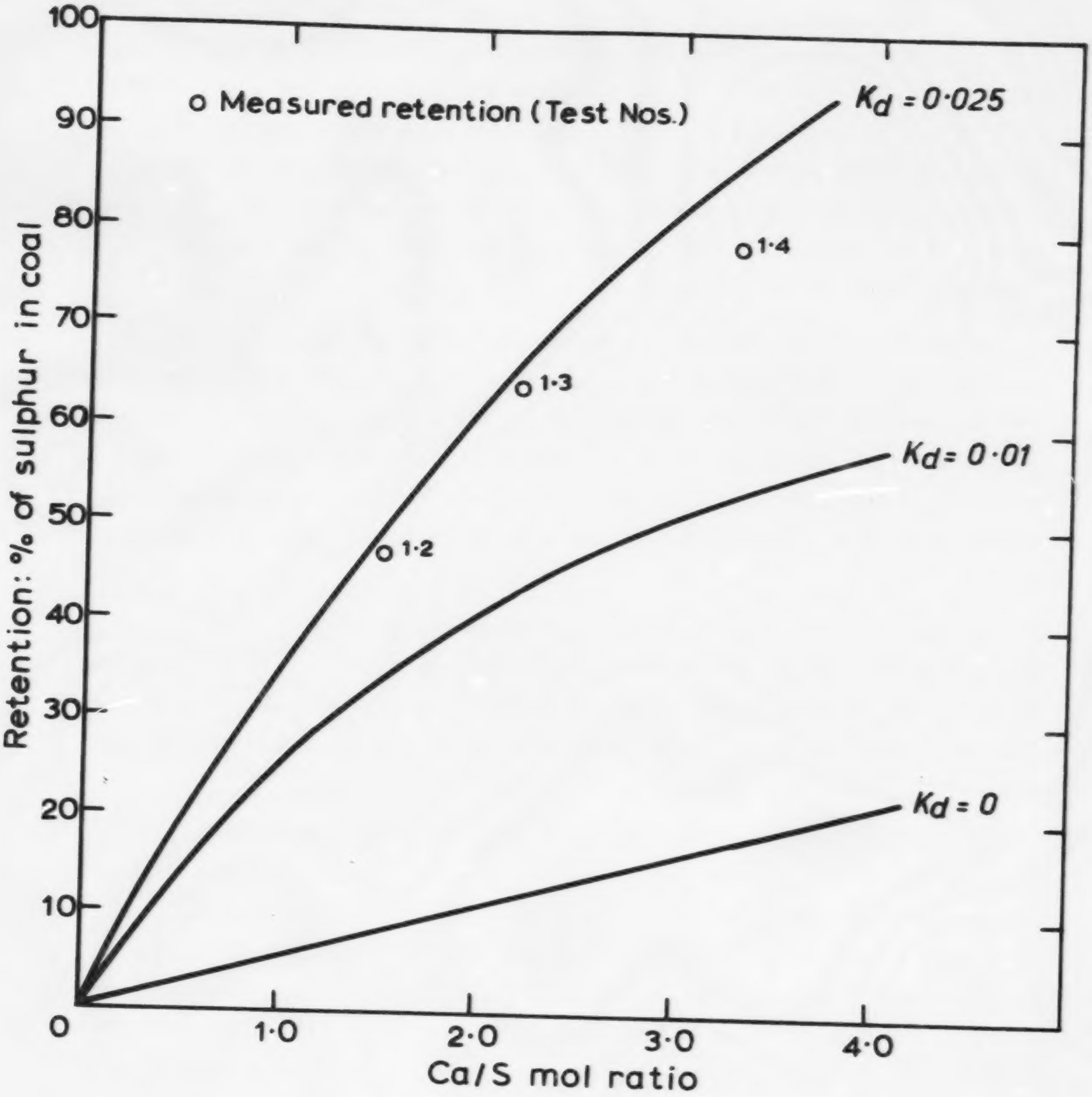


Fig. 7.25 Comparison of predictions for Limestone 1359 wit experimental results of Task V, showing effect o increasing attrition rate constant, K_d (n = 1)

In most of the computations it was assumed that all of the SO_2 was released at the bottom of the bed. Lower SO_2 reductions were predicted when it was assumed that SO_2 was released throughout the bed, particularly at high Ca/S mol ratios, Fig. 7.26. SO_2 release throughout the bed is thought to be the reason for the reduction being less than 100% in tests with Ca/S mol ratios of 5 at a fluidising velocity of 8 ft/s (36 in combustor, Test Series 6, Table 4.6).

The effects of varying bed depth and throughput (velocity) are shown in Fig. 7.27. The model predicts an improvement in retention on deepening the bed, mainly due to the increase in solids residence time when the bed is deeper. The residence times for non-elutriated solids corresponding to curves C, D and E in Fig. 7.27 are: 11 h, 21 h and 30 h respectively, allowing utilizations of 59, .71 and .78 respectively at a Ca/S mol ratio of 1.1.

The effect of increasing throughput is the reverse of that of increasing bed depth, mainly because of the reduction in particle residence time. There is an additional effect (relatively small in the case tested, but which could possibly be large) due to increased elutriation from the bed at the higher gas velocities involved.

. Reaction rate measurements for a range of temperatures were only determined for one stone, Limestone 18, Fig. 7.28. These showed that whereas unsulphated stone increased slightly in reactivity as the temperature was raised from 1472°F to 1652°F, stone of 20% utilization or more decreased in reactivity in this range. This rate data has been used in conjunction with other input data corresponding to tests on the 36 inch combustor, with the results shown in Fig. 7.29. A maximum of retention is predicted at about 1472°F in good agreement with experimental findings (Section 7.1.4).

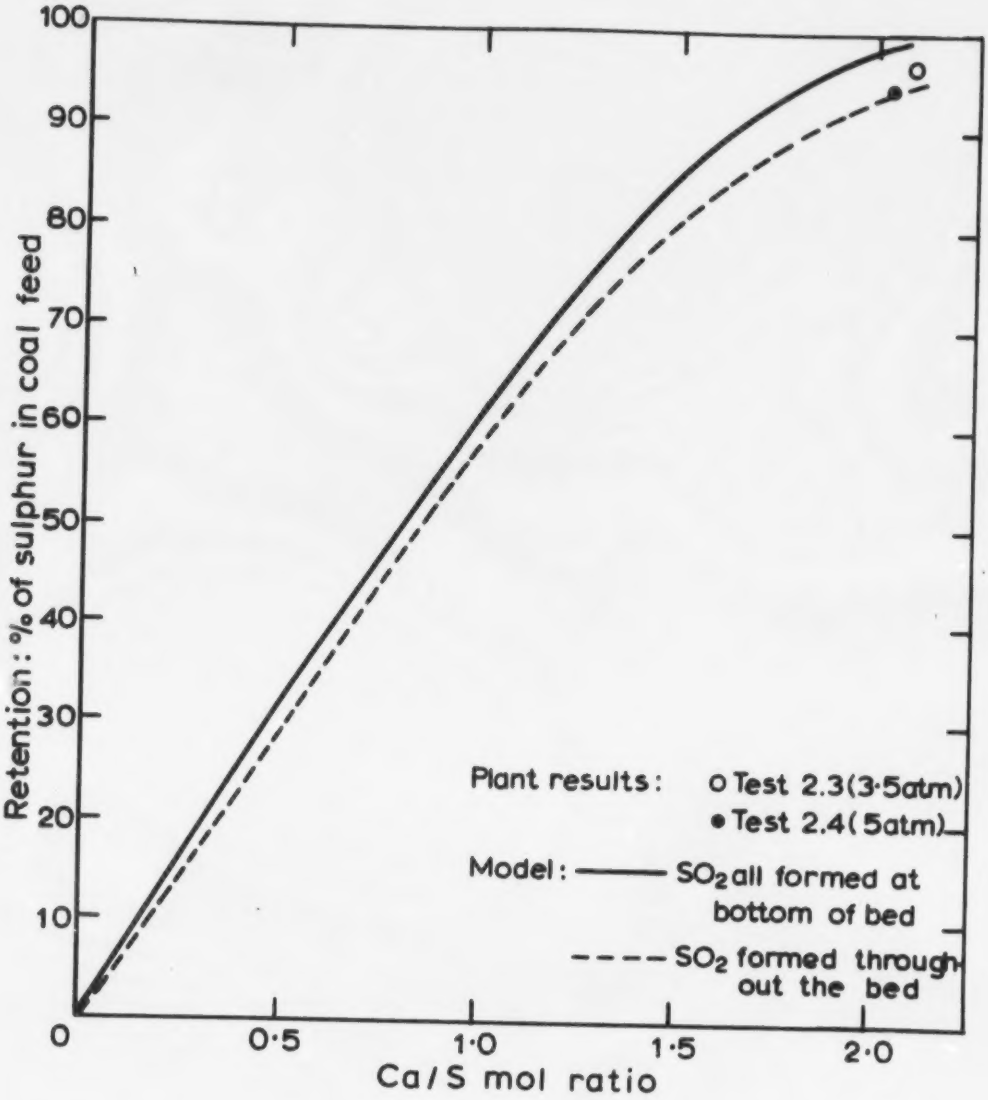


Fig. 7.26 Comparison of predictions for Dolomite 1337 with experimental results of Task II showing the effect of SO_2 release through the bed

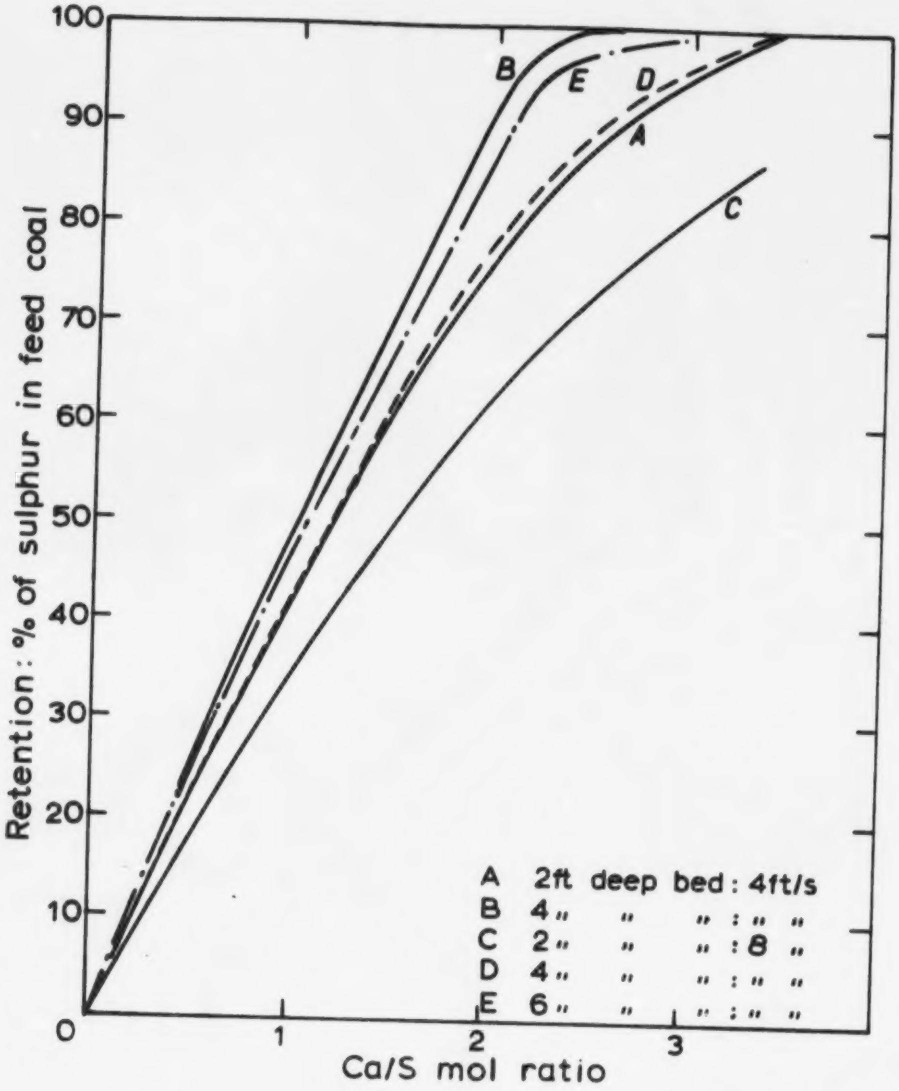


Fig. 7.27 Predicted effect of operating conditions for Limestone 18 (K_d =.025, n = 3)

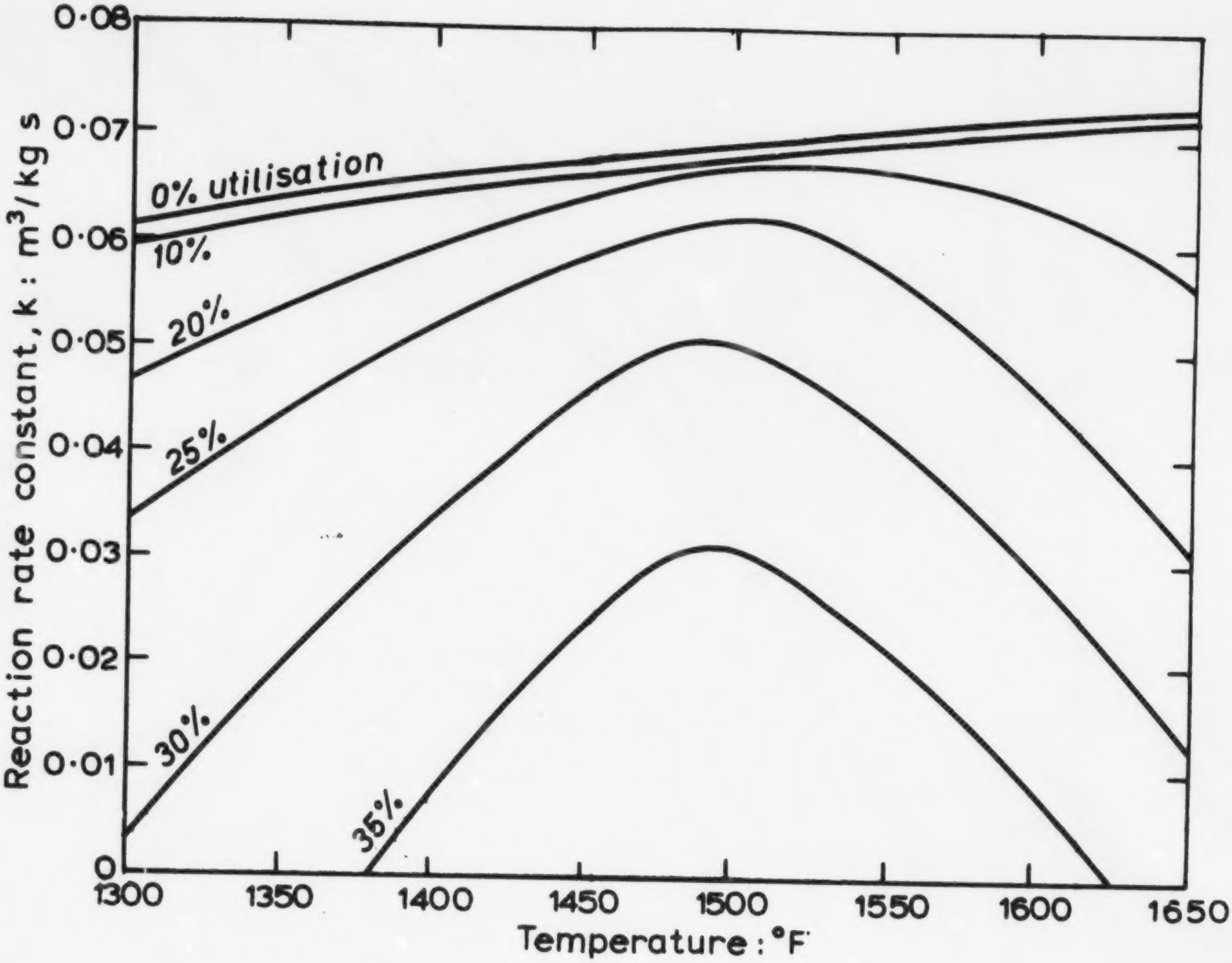


Fig. 7.28. Variation of reaction rate constant with temperature and % utilisation of limestone: Limestone 18 (−2060 +1000 μm)

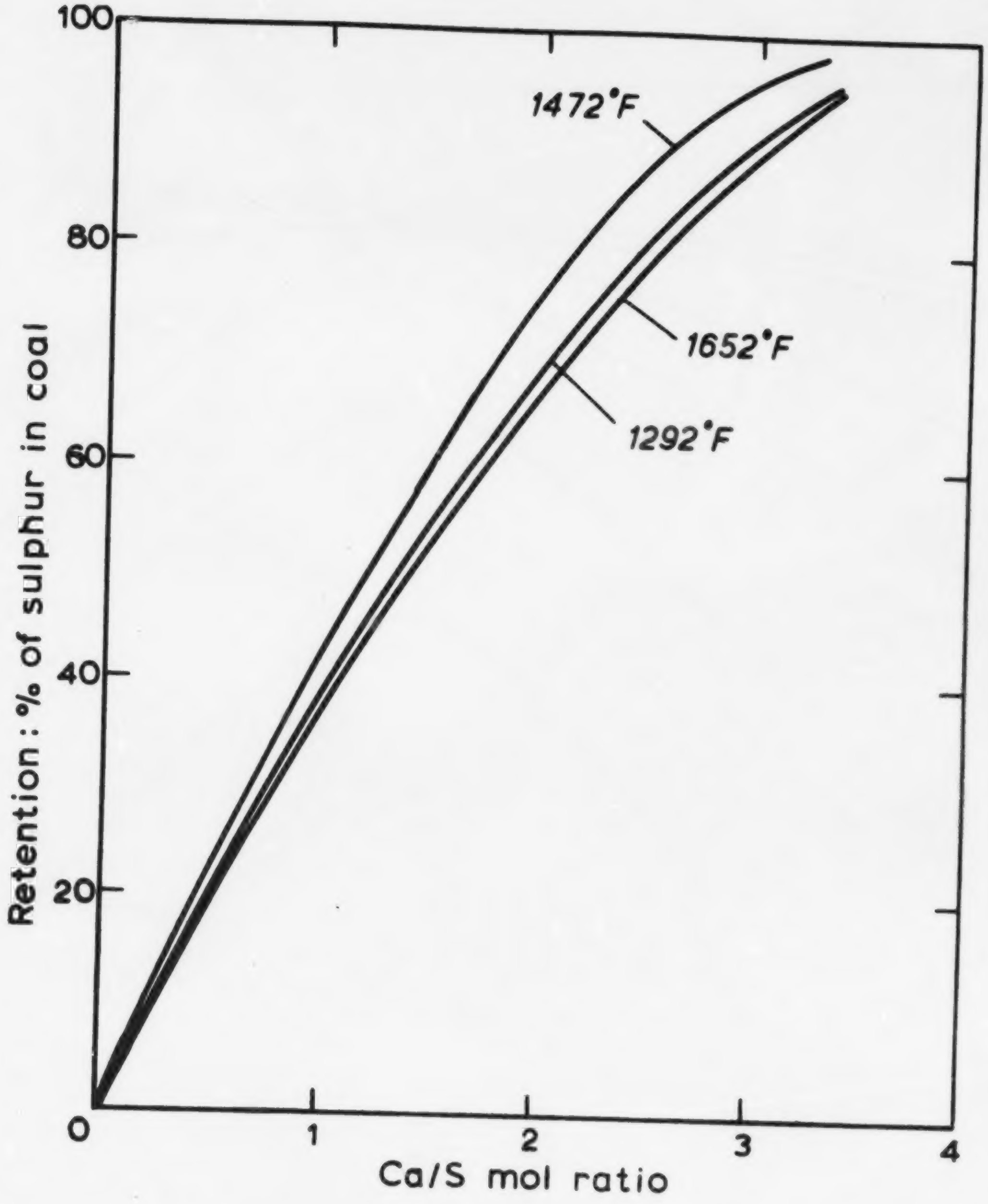


Fig. 7.29. Effect of temperature on sulphur retention predicted by mathematical model: Limestone 18 in 36in Combustor

7.2 Emission of nitrogen oxides

Since the infra-red absorption NO_x analysers ordered for this work were not delivered in time to be used, it was not possible to follow the variation in NO_x emission with changing operating conditions. However determinations of the NO_x concentration in the off-gas were made using the two methods described in Section 4.1.2 and Appendix 9, namely the modified Saltzman chemical analysis and the BCURA NO_x Box. In the data presented in Appendices 1, 2 and 3 the method of determination used is specified, but the agreement between the two methods was so close that the mean values only are given in the tables of Section 4.

About 80% of the NO_x determinations made in the 27 in and 36 in combustors were within the range 300 to 600 ppm v/v. Attempts were made to correlate the variations within this range with the plant operating conditions but there was no correlation with fluidising velocity, bed temperature, Ca/S mol ratio or SO_2 emission. However, in the 36 in combustor there was a tendancy for the NO_x concentration to increase as the SO_2 emission was reduced in some of the test series (Tables 4.4 and 4.6). Also some results (36 in combustor, Test Series 4, Table 4.6) indicate that the NO_x emission may be reduced by about 100 ppm when the coal size is reduced from -3175 to -1680 μm.

The NO_x emissions from the 48 in x 24 in pressurised combustor were significantly lower than those from the atmospheric pressure combustors (40 to 190 ppm, Table 4.9) but no reason can be confidently assigned for this. The highest NO_x concentrations were obtained at the lowest SO_2 emission levels but this may be due to chance.

7.3 Alkali and Chloride Emission

The presence of volatilised alkali in flue gases is believed to be important in the formation of alkali-rich deposits on superheater tubes in conventional boilers, although the mechanism of deposition is not clearly understood.

Measurements of the concentrations of volatilised sodium and potassium in the flue gases were made in tests in the 48 in x 24 in combustor and the 12 in combustor using electro-static precipitators as described in Appendix IV and by Ounsted[11]. A small cyclone, normally used in this method to remove very fine dust particles before the sampled gases are passed through the electro-static precipitators, was omitted in the 12 in combustor tests when it was found that no dust was being collected. It is assumed that the volatilised alkalis are present as sub-micron aerosols. Chloride in the off-gases was determined in tests in the 36 in, 48 in x 24in and 12 in combustors.

In the pressure combustor, the volatilised Na content of the gases was 1 to 2 ppm by weight, representing 1 to 2% of the Na input when burning Pittsburgh coal, and less than 1% of the input when burning Welbeck coal which has a higher Na content. The volatilised K content of the gases was less than 0.5 ppm by weight representing 0.2 to 0.3% of the K input. When limestone was used as the additive, the Na and K contents of the gases were 5 ppm and 1.5 ppm by weight, representing 3% and 1½% of the inputs respectively.

Alkali emissions from the 12 in combustor, both with and without limestone addition, were generally higher - 4 to 6 ppm by weight of Na and 1 to 3 ppm by weight of K, representing about 5% and 1%, respectively, of the Na and K input. These slightly higher emissions could be due to the slightly higher temperatures (1560°F compared with about 1470°F in the pressure combustor) or it could be that dolomite (used for most of the tests in the pressure combustor, but not in the 12 in combustor) inhibits the emission of alkalis.

Emissions from conventional plant have not been systematically investigated, but Na emissions of 10 to 40% of the input have been reported (Ounsted[11]). The considerably lower emissions obtained with fluidised combustion are due to the lower operating temperatures.

In the 12 in combustor the Na and K contents of the dust collected by the gas-cleaning cyclone and of the dust escaping the cyclone were similar to those in the coal ash (i.e. no enrichment occurred). The same was true of the dust collected by the two-stage gas cleaning system in the pressurised combustor but the dust escaping the second-stage cyclone showed higher contents of both Na and K (typically contents increased from 0.5% to 1% and from 0.7%

to 1.6% respectively) compared with the coal ash. Earlier work (Bethell[12]) showed that the Na can be concentrated slightly in the finer fractions of the ash.

The chloride content of the flue gases was typically 60 ppm by weight when burning Pittsburgh coal, representing (as expected) about 70% of the input chlorine, and 500 ppm when burning Welbeck coal (which has a higher chlorine content), representing more than 90% of the input chlorine. Measured values of the chloride content of the gases showed a wide variation (± 50%) but this reflects the difficulties inherent in the determination, and no correlation with operating variables could be found.

7.4 Combustion Performance

The combustion performance of a fluidised bed combustor is known to be affected by such operating parameters as excess air level, fluidising velocity and fines recycle. In order to simulate conditions in a boiler it was decided that tests would be carried out as far as possible with oxygen concentration in the off-gas in the range 2.5 to 3.5%. If combustion of the feed coal were complete, this would correspond to an excess air level of 12 to 18%. With operating conditions at which combustion was incomplete, e.g. high velocities without fines recycle, it was necessary to increase the coal feed rate in order to maintain combustion rate. This higher coal feed rate caused a reduction in the excess air level and in some cases substoichiometric feed rates were reached. The excess air levels have been calculated from the mass balances given in the Appendices, and typical results are given in Table 7.10.

For Pittsburgh coal in the 36 in and 6 in combustors (Tasks I and V) without fines recycle, the carbon loss at fluidising velocities in the range 2 - 4 ft/s was about 8%. The carbon loss was not affected by bed temperature, but more combustion occurred in the freeboard at lower bed temperature. Increasing the fluidising velocity to 8 ft/s caused a significant fall in combustion efficiency, resulting in carbon losses in the range 13 to 19%. At 2 ft/s in the 36 in combustor, the carbon loss was reduced to 1% by total fines recycle from a cyclone with a cut size of 10 μm.

Carbon losses from the pressurised combustor (Task II) were in the range 1 - 3%, the lower value being most frequently obtained with the high rank coal. Very little combustion occurred in the freeboard of this combustor, most probably as a consequence of the configuration of the tubes at the top of the bed which limited splashing.

Table 7.10

Effect of operating conditions on the loss of unburnt carbon

Coal	Pittsburgh								
Task	I							II	
Test	4.5	4.6	1.4	1.1	5.1	2.1	5.4	2.2	4.1
Fluidising velocity, ft/s	2	2	4	4	4	8	8	2	2
Bed temperature, °F	1470	1470	1380	1470	1560	1560	1560	1460	1460
Fines recycle	No	Yes	No	No	No	No	No	Yes	Yes
Pressure, atmospheres	1	1	1	1	1	1	1	3.5	5
Excess air, %	7	16	14	15	9	3	-4	22	18
% Unburnt carbon	8	1	8	8	8	13	19	3	1

Coal	Pittsburgh								
Task	III						IV		V
Test	2.3	2.12	2.4	3.1	3.2	3.4	2	3.2	4.2
Fluidising velocity, ft/s	8	8	8	6	11	11	3	3	3
Bed temperature, °F	1560	1560	1560	1525	1570	1550	1560	1560	1470
Internal fines recycle	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	No
External fines recycle	Yes	Yes	Yes	Yes	Yes	No	–	–	–
Excess air, %	-4	1	4	-5	9	7	5	12	4
% Unburnt carbon	16	12	9	11	9	15	7	1	9

Coal	Welbeck							Illinois		Park Hill
Task	I		II	V				V		V
Test	3.6	3.3	1.3	2.1	2.8	2.4	5.2	3.1	3.3	2.10
Fluidising velocity, ft/s	4	8	2	2	2	3	3	3	3	3
Bed temperature, °F	1560	1560	1460	1470	1470	1470	1470	1290	1470	1470
Fines recycle	No	No	Yes	Yes	No	No	No	No	No	No
Pressure, atm	1	1	3.5	1	1	1	1	1	1	1
Excess air, %	10	10	22	15	10	10	2	7	10	4
% Unburnt carbon	6	9	2	3	5	8	12	7	5	9

In Test 2 of the 12 in combustor (Task IV) the recycle system was nominally in operation, but it is thought that the good agreement with those tests without recycle in the 36 in and 6 in combustors indicates that the recycle system was malfunctioning. The carbon loss of 1% with fines recycle in Test 3.2 in the 12 in combustor is in good agreement with tests in the 36 in and the 48 in x 24 in combustors.

Even with internal and external fines recycle in the 27 in combustor, the carbon loss was of the same order as in the other combustors without recycle. The poor combustion efficiency is thought to be due to quenching of combustion in the freeboard by the water cooled walls.

From combustion efficiency considerations the losses of combustible gases in all but the 27 in combustor were negligible, comprising less than 200 ppm of CO in the off-gas. However in the 27 in combustor there was about 0.6% of CO in the off gas, equivalent in heat loss to about 3% unburnt carbon.

Typical carbon losses for the three other coals are given in Table 7.10. These results indicate that there is little difference between the combustion performance of the four coals used.

7.5 Emission of Particulates

Particulate matter emitted from fluidised bed combustors consists of unburnt carbon, ash and additive particles. For a combustor operated without fines recycle the carbon elutriated from the bed represents 5 to 15% of the feed coal, and 80 to 100% of the ash and additive is also elutriated. Almost all of these fines can be collected by efficient cyclones. In the 36 in and 12 in combustors the primary and secondary cyclones were 90% efficient at about 10 μm, and particulate emissions were in the range 0.1 to 0.6 gr/scf, representing 1 to 5% of the non combustible material in the feed. In the pressurised combustor, which had an extra cyclone, the dust loading at the turbine cascade was only 0.05 to 0.1 gr/scf. Particulate emission from the 27 in combustor was an order of magnitude higher because the cyclone efficiency was lower.

The emission increased approximately in proportion to the feed rate of ash plus additive. There was little effect of fluidising velocity; although there was increased elutriation at higher fluidising velocities, the cyclones operated more efficiently and there was thus no increase in emission.

In order to achieve a satisfactory combustion efficiency it is necessary to burn the elutriated carbon fines, either by recycle to the main bed or by separate firing to a burn-up cell. Both of these methods, but particularly fines recycle, will result in an increase in particulate emissions since the ash and additive fines have to be re-collected. In the 36 in combustor the particulate emission increased to 1.4 gr/scf when the primary cyclone fines were recycled to the bed.

Based on these results it is unlikely that there would be any problem in meeting projected statutory limitations on particulate emission.

7.6 Corrosion and deposition

7.6.1. Deposits

Under normal operating conditions, the amount of material adhering to the tube surfaces was negligible. The slight accumulations which occurred on tubes near coal nozzles or on tubes above the bed generally had the same composition as the ash, although in some isolated instances there was a slight enrichment in alkalis or sulphur.

This fredom from deposition as compared with conventionally-fired boilers is thought to be due to:-

(a) the lower vapour pressures of the alkali salts at the lower temperatures in the fluid bed and consequently the reduced tendency for volatilisation of the alkalis. This is in contrast with conventional pulverised coal-fired boilers where flame temperatures are about 2900°F and where the fireside deposits that form are frequently enriched with sodium, potassium and sulphur;

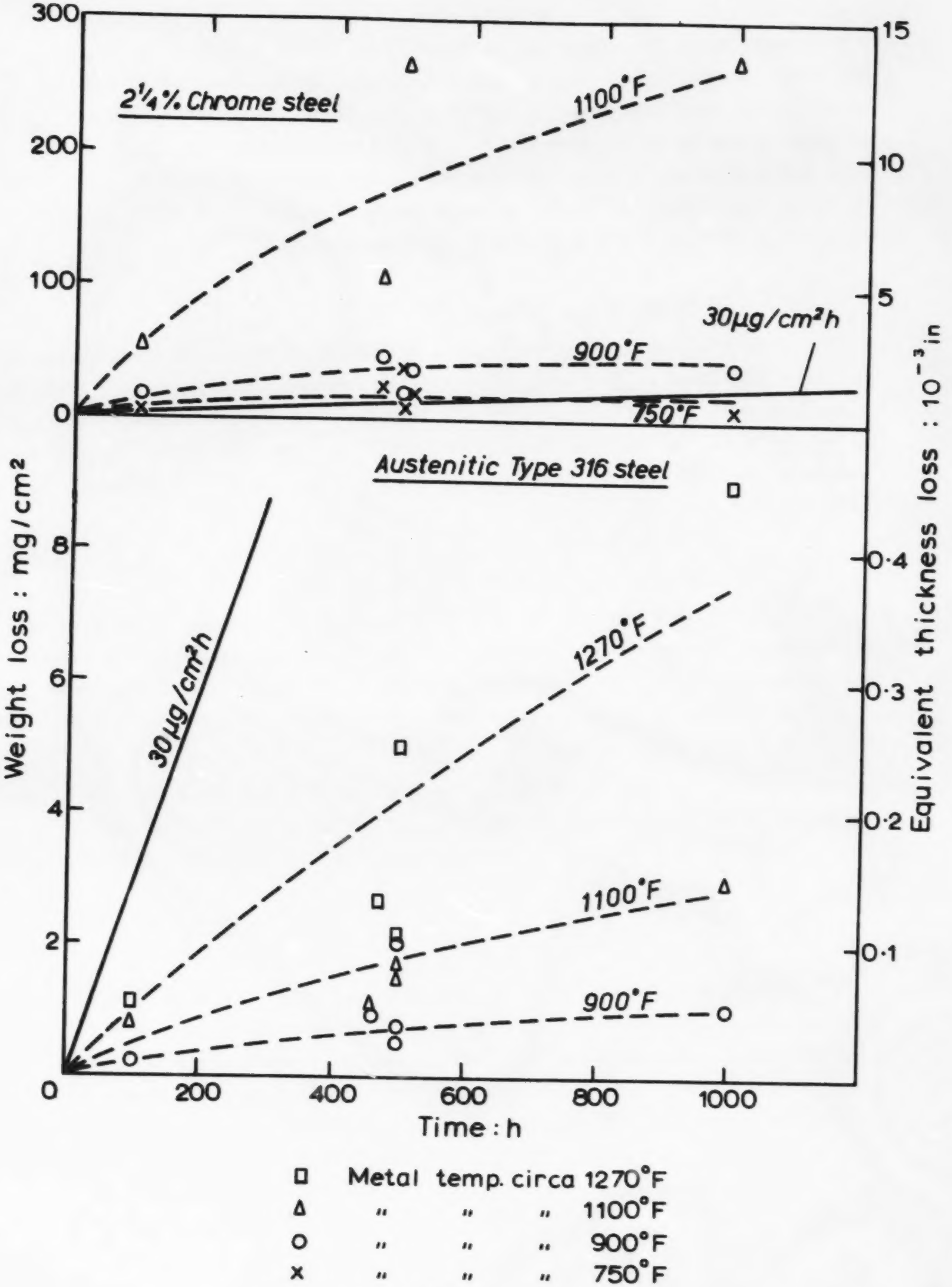
(b) the 'scouring' action of the fluidised bed.

The former is probably the more important factor.

7.6.2. Corrosion

7.6.2.1. Effect of time

Figure 7.30 shows the average specimen weight loss of a typical low alloy steel (2¼% Cr) and a typical austenic steel (AISI 316) as a function of time for tests with Pittsburgh coal. Results for 12% Cr steel were similar to those for the austenitics. On each graph a line indicates the 30 $\mu g/cm^2h$ rate of metal wastage which is assumed to be tolerable.


2¼% Chrome steel
300
200
100
0
15
10
5
1100°F
900°F
750°F
30μg/cm²h
Austenitic Type 316 steel
8
6
4
2
0
0·4
0·3
0·2
0·1
30μg/cm²h
1270°F
1100°F
900°F
200
400
600
800
1000
Weight loss : mg/cm²
Equivalent thickness loss : 10⁻³ in
Time : h
□ Metal temp. circa 1270°F
Δ " " " 1100°F
O " " " 900°F
x " " " 750°F

It will be seen that the rate of metal loss is non-linear with respect to time. This is somewhat academic for the 12% Cr and austenitic steels where metal loss rates are extremely low, but is important for the low alloy steels. There can be little doubt that these steels would have an acceptable rate loss over the life time of a boiler (e.g. 100,000 hours) at temperatures up to at least 900°F. It is also probable that the rate loss would be acceptable for 2¼% Cr steel at near its normal maximum operating temperature of 1090°F, although tests of longer duration (i.e. longer than 1000 h) would be needed to prove this point.

7.6.2.2. Effect of different coals

In addition to Pittsburgh coal, Welbeck (0.5% Cl content) was burned in Test 1 of the 48 in x 24 in pressurised combustor. Comparisons with Tests 3, 4 and 5 show little difference in weight loss rates for the two coals. This is in line with earlier evidence obtained on the 12 in combustor suggesting that the nature of the coal does not have a major effect on corrosion in fluidised combustion.

7.6.2.3. Effect of fluidising velocity

It was mentioned in the introduction that the effect of erosion by the fluid bed ash particles was not known. Erosion might prevent deposit formation and so reduce corrosion or it might accelerate attack by preventing the formation of a protective oxide film. In the work reported here, wastage could in no case be attributed directly to erosion.

It is possible to compare the weight losses after 500 h tests in 12 in and 27 in combustors in which the fluidizing velocities were 3 and 8 ft/s respectively. The results show some scatter but do not indicate any marked effect of fluidising velocity.

7.6.2.4. Effect of operating pressure

A comparison of the results from 100 h tests in the 48 in x 24 in combustor (at 3.5 to 5 atm pressure) and 12 in combustor (at atmospheric pressure) taken together with earlier evidence shows that weight loss measurements are in reasonable agreement, as are the results of metallographic examinations. It is concluded that pressure does not affect the corrosion of tubes immersed in the bed.

TABLE 7.11

Comparison of Weight loss Data from 500 h Tests With and without Limestone Addition (12 in Combustor)

Alloy	Nominal Tube Wall Temp °F	Position	Wt. loss rate, $\mu g/cm^2$ h	
			Without Limestone	With Limestone
Medium carbon steel	750 750 930	In bed Above bed In bed	48 25 88	41 18 84
$2^{1}/4$% Cr, 1% Mo	750 750 930	In bed Above bed In bed	32 25 78	42 18 98
12% Cr	1320 1320	In bed Above bed	3 1	7 2
AISI 316	1320 1320	In bed Above bed	4 1	6 2
AISI 347	1320 1320 1560	In bed Above bed In bed	3 1 7	6 2 3
Esshete 1250	1320 1320 1560	In bed Above bed In bed	6 5 7	13 6 3
PE 16	1320 1320 1560	In bed Above bed In bed	3 1 3	5 2 2

7.6.2.5. Effect of additive

The effect of limestone addition on metal wastage in the 12 in combustor is shown in Table 7.11, where the average specimen weight losses in the two 500 h tests with and without limestone addition are given. The overall picture confirms that there was little difference in metal wastage between the two tests.

Microscopic examination of specimens from the two 500 h tests indicates that there was more attack of specimens which had been tested with limestone addition. Particularly with the high chromium steels at 1100°F, 1320°F and 1560°F somewhat more sulphide penetration (up to 40 μm) had occurred. It is possible that limestone feed to the bed resulted in more sulphide penetration of the alloys, because of the higher sulphur potential in the bed. However, sulphide attack, of the same amount as reported here, was also found in earlier tests with Newstead coal and no limestone addition.

Limestone or dolomite addition to the pressurised combustor produced similar results, the weight losses showing little change and the metallographic examination showing a slight increase in sulphur penetration.

7.6.2.6. Comparison of 'above bed' and 'in bed' results

Tubes above the bed are in less intimate contact with ash and carbon particles, and as might be expected, weight losses for specimens placed above the bed were substantially lower than those situated in the bed.

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Task I	The project leaders were D.C. Davidson and D.F. Williams: A.A. Randell was responsible for operation of the plant: D.G. Cox and J. Highley carried out the data processing and assessment of results.
Task II	The project leader was A.G. Roberts: D.M. Wilkins was responsible for operation of the plant and J.E. Stantan carried out the data processing and assessment of results.
Task III	The project leader was D.J. Loveridge: M.H. Barker was responsible for operation of the plant and D.M. Wilkins carried out the final data processing and assessment of results.
Task IV	The project leader was M.J. Cooke: B.J. Bowles was responsible for operation of the plant; E.A. Rogers carried out the corrosion studies.
Task V	The project leader was D.C. Davidson: A.W. Smale was responsible for operation of the plant; D.G. Cox, J. Highley and J. Holder carried out the data processing and assessment of results.
Task VI	The project leader was D.W. Gill: he was assisted by F.V. Bethell and B.B. Morgan.
Task VII	The project leader was D.C. Davidson: the experimental work was carried out by R.F. Littlejohn.
Task VIII	The project leader was D.H.T. Spencer: he was assisted by A.A. Herod and B.A. Napier. Additional work to obtain data for the mathematical model was carried out by F.V. Bethell and G. McDonald.

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10. Glossary

Ca/S mol ratio:	$\dfrac{\text{Mols of calcium in additive}}{\text{Mols of sulphur in coal}}$
Sulphur retention:	$\dfrac{\text{Sulphur in coal} - \text{Sulphur in gas}}{\text{Sulphur in coal}} \times 100\%$
SO_2 reduction:	$\dfrac{SO_2 \text{ emission without additive} - SO_2 \text{ emission with additive}}{SO_2 \text{ emission without additive}} \times 100\%$
Absorption ratio:	$\dfrac{SO_2 \text{ reduction}}{100 - SO_2 \text{ reduction}}$
Utilisation of additive:	$\dfrac{\text{Mols of sulphur retained by additive}}{\text{Mols of calcium in additive}} \times 100\%$
Fluidising velocity:	$\dfrac{\text{Volume flow rate of gas at combustion temperature and pressure}}{\text{Cross section of combustor (neglecting tubes)}}$
Excess air:	$\dfrac{\text{Air input} - \text{Stoichiometric air for coal input}}{\text{Stoichiometric air for coal input}} \times 100\%$
Unburnt carbon loss:	$\dfrac{\text{Unburnt solid carbon}}{\text{Carbon in coal input}} \times 100\%$